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PART II: APPENDIX

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Sampling and analysis was designed to determine ambient concentrations of ethylene dibromide and other brominated chemicals near production facilities in El Dorado and Magnolia, AK. A characterization was made of the environmental matrices - air, water, soil, sediment and biota - for the presence and levels of ethylene dibromide, vinyl bromide and other related chemicals surrounding the bromine industry.

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ENVIRONMENTAL MONITORING NEAR INDUSTRIAL SITES: BROMINATED CHEMICALS

PART II: APPENDIX

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SECTION A: ANALYTICAL PROTOCOLS

A. SCANNING ELECTRON MICROSCOPY (SEM) AND ENERGY DISPERSIVE X-RAY ANALYSIS (EDX)

1.0 Principle of Method

When a finely focussed beam of electrons is scanned across a solid, low energy secondary electrons that are emitted may be detected with a scintillator and the resultant "light" amplified with a photomultiplyer. This output is synchronized in time with the scanning beam of electrons and the result displayed on a cathode ray tube, and forms the principle of the scanning electron microscope. Similarly emitted X-rays characteristic of the elements in the solid sample can also be detected, converted to specific charges, amplified and sorted out with a multichannel analyzer. As the beam of electrons scans the sample only X-ray photons contributing to a particular channel or channels may be synchronously displaced on another CRT. This is conventionally referred to as "X-ray mapping." Thus when a filter containing various particulates or adsorbed material is placed in the instrument, the elemental composition and distribution can be recorded as well as an electron micrograph of the surface.

2.0 Sensitivity and Range

The microscope is capable of resolving objects ranging in size from 1 cm down to 10 nm. The EDX system is sensitive to overall concentrations of elements of higher atomic number 10 in ranges down to between 100 and 1,000 ppm depending on the particular element. However, it can also resolve particulates down to about 300 nm in the mapping mode and about 80 nm if the beam is very finely focussed and stationary (probe or spot mode).

3.0 Interferences

Pollutants were collected on either glass or cellulose filters. Small (approx. 25 mm^2) samples were mounted with colloidal graphite (Aquadag) on spectroscopically pure carbon microscope stubs. Therefore, there was always a background from the constituents of the filters plus the carbon stub. There was also some additional background from the chamber itself; this was Al, Si and Ni with a trace of Cu and Fe. On the glass filter the predominant interferences were Na, Mg, Si with traces of K and Ca, together with the continuous radiation from the carbon stub. The cellulose filter showed much less characteristic peaks, the main one being Ni with traces of Al, Si, Fe and Cu superimposed on the cellulose and carbon continuous radiation.

4.0 Precision and Accuracy

The interferences noted in 3.0 will all affect the limits of detectability of those particular elements. Other elements will only be affected by the continuous backbround. Thus it was easy to map a particle of about 5 micron^2 of calcium but not possible to localize bromine, although one could detect the latter. It was also possible to map silicon even on the glass substrate because the concentration was higher than that of the substrate. It should be noted that this method is purely qualitative under the described conditions and no conclusions may be drawn concerning the amounts of material present. For such determinations using this methodology samples would have to be prepared under totally different conditions to take account of topography, matrix effects, instrument calibration etc.

5.0 Apparatus

5.1 Sample Collection:

Hi-Vol Sampler (ex. GMW1 2000, General Metal Works, Inc. Cleves, Ohio)

Glass Fiber Filters

Whatman No. 1 Filters - washed three times with deionized water,

or

Pump (ex. Nutech Model 221A, Nutech Corp., Durham, NC)

Filter Holder (ex. Gelman 1107)

Glass Fiber Filters

Whatman No. 1 Filters - washed three times with deionized water

5.2 SEM/EDX Analysis

ETEC Autoscan Scanning Electron Microscope

KEVEX 5100 Energy Dispersive X-ray Spectrometer

Spectroscopically Pure Carbon Stubs (SPI Supplies Inc., West Chester, Pa.)

Colloidal Graphite (Aquadag) for mounting specimens to stubs.

Carbon Evaporator (JEOL Vacuum Evaporator)

Carbon rods (1/4" diameter)

Polaroid 55 P/N film for recording spectra and micrographs

2 Polaroid cameras.

6.0 Procedure

Spectra are obtained from blank (unexposed) glass and cellulose filters which may or may not be lightly carbon coated to reduce charging in the SEM. Beam current is set to approx. 10^{-9} amps, take-off angle approx. 45°, tilt 30°, working distance 15 mm. Under rapid scanning conditions (*e*.*g*., TV speeds) this will give a spectrum of about 250,000 counts in about 2 minutes and enables the background to be assessed.

The protocol then can be varied depending on the state of the investigation, i.e., whether it is a preliminary survey of all the elements detectable or whether one is interested in a particular species.

The procedure to date has been to gather data as an overall survey of the elements present. To this end spectra are recorded at low magnification so as to include the majority of the sample under the conditions for the control above. The samples are then viewed at increasingly higher magnifications until particulates are seen. The scanning raster is then located over these particulates and the spectrum noted. All the major peaks other than normal background are then sequentially selected for mapping using the appropriate channels of the multichannel analyzer, and the resultant X-ray map photographed from the display CRT. In this way, elemental distribution maps can be built up and finally the same area is photographed in the SEM mode. Thus certain morphological entities may be identified as to their elemental composition. This procedure is repeated on other regions of the sample until a consistent picture is built up.

It should be noted that there is no standard procedure for the time of exposure to obtain maps. This is usually assessed visually in order to obtain an unambiguous distribution of counts, but on the average, under the above beam conditions, will it take about 4 to 16 minutes per map, and 60 sec to obtain the scanning electron micrograph.

Background maps from off-peak positions are also taken as a control when weak maps (low count statistics) are encountered.

7.0 References

1. D. R. Beaman and J. A. Isasi, "Electron Beam Microanalysis," Publication 506, American Society for Testing and Materials, Philadelphia, Pa., 1972.

B. TOTAL BROMINE AND CHLORINE BY NEUTRON ACTIVATION ANALYSIS

1.0 Principle of the Method

A sample which contains the element(s) of concern contains the isotopes of that element in approximately their natural abundance. This usually means they are predominantly stable or nonradioactive isotopes. If this sample is placed in a neutron flux the nuclei of the element(s) will adsorb additional nuclei which can result in the conversion of the stable isotope into a radioactive one. The radioactive decay provides the means for identifying and quantitating the element. The qualitative parameters are the energy of the radiation emitted and the lifetime while the quantitation is based on the number of decompositions per unit time under standardized conditions (i.e., neutron flux, time of irradiation, time between irradiation and observation and counting efficiency).

2.0 Range and Sensitivity

Quantitation can be made from essentially pure material down to 15 ng/g for bromine and 50 ng/g for chlorine.

3.0 Interferences

Some interference from high levels of sodium and potassium are encountered. Standardization for possible matrix effects must be made.

4.0 Precision and Accuracy

Precision and accuracy will depend upon the magnitude of matrix effects of their reproducibility.

5.0 Apparatus

Nuclear reactor to provide neutron flux.

Equipment for handling radioactive material.

Gamma Counter with a multi-channel analyzer for energy discrimination.

6.0 Procedure

A weighed sample is heat sealed in a 1 ml or 5 ml polyethylene or quartz irradiation vial. The sealed vials along with similarly sealed standards of the elements to be analyzed are irradiated in the reactor for a predetermined neutron fluence. After irradiation, the samples and standards are counted on a solid state detector connected to a multi-channel analyzed to permit identification and quantitative analysis.

7.0 Calibration

Standards are used in the procedure to calibrate the method. In addition, quality assurance standards prepared using sodium bromide or chloride are submitted for analysis with the samples.

8.0 Calculations

8.1 Bromide as Br^-

$$\mu g\ Br^-/M^3 = \frac{\mu g\ Br^-/g \times g\ \text{total material}^*}{M^3\ \text{sampled}}$$

*Total weight of filter impinger solution, or sorbent material.

8.2 Chloride as Cl^-

$$\mu g\ Cl^-/M^3 = \frac{\mu g\ Cl^-/g \times g\ \text{total material}}{M^3\ \text{sampled}}$$

Analytical protocol revised 1/24/77.

C. ANALYSIS FOR ETHYLENE IN AMBIENT AIR

1.0 Principle of Method

Atmospheric ethylene is identified and quantitated by gas chromatography. The air sample is introduced into a chromatographic column consisting of a OV-101 SCOT using helium as a carrier gas. This gas stream is then introduced into a hydrogen-oxygen flame ionization detector. The hydrocarbon molecules are ionized in the intense heat of this flame. The ions are are then collected at the electrodes and the resulting current is measured by an electrometer.

The electrometer is connected to a strip chart recorder which records the response (as a function of time) of the flame ionization detector as ethylene is eluted from the chromatographic column. The area of the peak on the strip chart recorder is used to quantitate the ethylene, where this area is calculated as height times the width at one-half the peak height (generally the peak width is constant and peak height only can be used).

The method is rapid and especially applicable to routine sampling analysis for both "grab" and integrated samples. The elution order for the hydrocarbons in the region of elution for ethylene are as follows: methane, ethane, ethylene, acetylene, propane, propylene, _n_-butane, isobutane, butene-1, etc.

2.0 Range and Sensitivity

The lower limit of measurement for the ethylene is ~0.01 ppm by volume (_i.e._, 0.01 $\mu\ell/\ell$). The upper limit of measurement is considered greater than the anticipated concentrations of ethylene in the ambient air.

3.0 Interferences

At the present time there are no known common pollutants in the ambient air in sufficient concentrations to interfere with the estimation of ethylene. However, in order to obtain representative atmospheric samples, the selection of the sampling site is most important. The selected site should be reasonable distant from local sources of hydrocarbon emissions and in a locale where the surrounding topography is conducive to adequate mixing of the ambient atmosphere. Under such conditions local source emissions will not bias the hydrocarbon data toward a specific individual hydrocarbon, more specifically ethylene.

4.0 Precision and Accuracy

Replicate analysis of aliquots of uniform air samples and known standard ethylene air vapor mixtures should not deviate by more than ±10% relative standard deviation using this procedure.

5.0 Apparatus

5.1 Chromatograph and Chromatographic Column

A glass SCOT capillary (0.35 mm x 60 m in length) coated with OV-101 stationary phase is used in a Varian Aerograph Model 1400 gas chromatograph. The column is commercially available from Perkin-Elmer Corp. The column is generally conditioned by passing the carrier gas through it for a minimum of two hours at a temperature of 220°. During operation, the column temperature is reduced to -60°C by introducing a fine spray of liquid nitrogen into the oven until the gaseous sample has been introduced and then programmed up to 100°C at 6°/min. The helium carrier gas flow through the column is ~5 ml/min.

5.2 Sample Injector

A six-way gas sampling valve (Valco, Houston, TX) with a 1.9 ml (1.7 mm i.d. x 842 mm long) stainless steel sampling loop is used. The length of the gas sampling loop is dictated by the ethylene concentration.

5.3 Detector

Hydrogen flow to the flame ionization detector is maintained at ~12 ml/min and the oxygen flow will be ~10 times the hydrogen flow (~150 ml/min).

5.4 Electrometer

A Varian Dual/Differential electrometer or equivalent is used.

5.5 Recorder

A Houston Instruments, Omniscribe® strip chart recorder with a range of 0-1 millivolt and a 1 sec response is employed.

5.6 Vacuum Samplers

Alumimum cannisters equipped with septum closures and having a capacity of 280 ml are used for sampling. These cannisters are evacuated to a pressure of <2 mm before deployment to the field. Two to three cannisters are transported to the field containing known concentrations of ethylene for control purposes. Two to three cannisters are transported containing helium for a check on potential contamination during transportation and storage.

5.7 Sample Injection

Samples are withdrawn from the vacuum cannisters with a 5 ml gas syringe equipped with a shutoff valve. Two, 5 ml aliquots of sample are injected through the gas sampling loop, the six-port, two position valve rotated and the sample introduced into the gas-liquid chromatograph.

6.0 Materials

OV-101 SCOT capillary (200 ft) - Perkin-Elmer Corp., Norwalk, CN.
Vacuum Samplers - Alltech Associates, Arlington Heights, IL.
5 ml Gas Syringe - Precision Sampling Corp., Baton Rouge, LA.
Ethylene - Matheson, Chicago, IL.

7.0 Procedure

7.1 Collection of Field Samples

Evacuated vacuum samples bags with an approximately 280 ml capacity are used to collect ambient air samples. Collection is achieved by insertion of a 22 gauge needle through the septum and allowing the cannister to fill for ∿2 minutes. This procedure represents the collection of "grab" samples.

7.2 Transport and Storage

Immediately prior to the collection of a sample, the vacuum in each cannister is tested with a vacuum gauge. Approximately 5% of the cannisters are found to have internal pressures >2 mm after approximately two weeks of storage. These cannisters are outfitted with new septa and re-evacuated. No evidence of ethylene losses or contamination is suggested for filled cannisters.

7.3 Range of Hydrocarbon Values Anticipated

Table C1 depicts the hydrocarbon values which have been determined in urban air masses. It is evident from this table that the concentration of ethylene can range from 0.004 ppm up to 0.3 ppm.

During the collection of the sample, observations are carefully recordered, *e.g.*, was there an intermittant source of hydrocarbon emissions such as an automobile starting, stopping or passing near the sampling site? If the sampling site is near a refinery or petroleum processing plant, was there a possible operationable upset that resulted in venting of unusual amounts of hydrocarbons? These situations can have a significant influence on the concentrations of hydrocarbons specifically ethylene. Other emission sources may be a possibility and must be noted if recognized particularly if they are

Table C1. RANGES OF HYDROCARBON VALUES IN SOME URBAN AIR MASSES

Component	Range, ppm in air	
	Minimum	Maximum
Methane	1.2	15
Ethane	0.005	0.5
Propane	0.003	0.3
Isobutane	0.001	0.1
n-Butane	0.004	0.4
Isopentane	0.002	0.2
n-Pentane	0.002	0.2
Ethylene	0.004	0.3
Propene	0.001	0.1
Butene-1	0.000	0.02
Isobutylene	0.000	0.02
Trans-2-butene	0.000	0.01
Cis-2-butene	0.000	0.01
1,3-Butadiene	0.000	0.01
Acetylene	0.000	0.2

not responsible for the emission of ethylene which is the objective of this project. As a general rule of thumb, if methane, ethane or propane concentrations are high relative to other identified hydrocarbons, then one should look for source emissions of natural gas. If acetylene and butenes are high, one should recognize the possibility of a nearby automobile exhaust source. If n-butane, pentane or isopentane are high, then one should be aware of a source of gasoline evaporation.

The cannister containing the collected sample is identified with a code and recorded according to the appropriate information, date, time of collection, location of sample collection, weather and other air pollution conditions, etc. It is not necessary to know the exact volume of the sample collected since the exact volume to be analyzed is taken during the gas chromatographic analysis step. The concentration of the ethylene in the ambient air is based on the volume of the sampling loop (1 ml or 5 ml) on the six-port valve affixed to the gas chromatograph.

8.0 Calibration and Standards

A calibration standard is prepared for ethylene. The retention time used for identification of this hydrocarbon and peak height or peak area is used for quantitation of ethylene. Standard calibration mixtures are based on a commercial source. Dilutions from the primary standard of ethylene are made in Tedlar® bags. This is accomplished by metering predetermined amounts of ethylene and nitrogen into a Tedlar® bag. Based upon the volume of gas introduced bag and the volume and concentration of the ethylene standard introduced, the final dilution is calculated. A series of dilutions is prepared in this manner.

Approximately 10-20 ml of the standard gas is flushed through the 1 ml (or 5 ml) stainless steel sampling loop of the six-port valve. One ml of the standard gas is then injected into the gas chromatograph. The response of the hydrogen flame ionization detector is linear from 0.01 to ~10 ppm.

9.0 Calculation

Air samples collected in the field and returned to the laboratory are calculated according to the following procedure. The response of the flame ionization detector is recorded on the strip chart recorder as ethylene is eluted from the column. The time of elution is recorded for each hydrocarbon as well as ethylene. Peak height is used for quantitating ethylene and the concentration is determined in the sample by using the calibration response factor: ppb hydrocarbon = f x peak response x attenuation, where f is the calibration response factor for ethylene (ppb/mm peak height), peak response is the peak height (mm) for ethylene and attentuation is the electrometer attenuation setting.

The response factor for ethylene at no less than three different concentrations is averaged and this response factor equals the concentration of the standard (ppb) divided by the detector response (mm) times the attentuation.

10.0 References

1. "Methods of Air Sampling and Analysis", Amer. Pub. Health Assoc., Washington, D. C., p. 131 (1972).
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Analytical protocol revised 7/15/77.

D. SAMPLING AND DIRECT ANALYSIS FOR METHYL CHLORIDE AND METHYL BROMIDE IN AMBIENT AIR

1.0 Principle of Method

Atmospheric methyl chloride and methyl bromide is quantitated by gas chromatography equipped with electron capture detection (1-3). The air sample is introduced into a chromatographic column consisting of a 10 ft x 1/8 in. stain steel Durapak n-octane/Poracil C (100-120 mesh) column. The carrier gas is nitrogen. The gas stream passes into an electron capture detector which measures the decrease in the thermal electron plasma level during the capture of an electron by an organic molecule (4). Both methyl chloride and methyl bromide undergo electron capture processes. The decrease in the plasma current is measured during the elution of compounds from the chromatographic column and the resulting current is amplified by an electrometer.

The electrometer is connected to a strip chart recorder which records the response of the detector as a function of time. The area of the peak for methyl chloride and methyl bromide on the strip chart recorder is used to quantitate these compounds (calculated as height x the width at 1/2 peak height).

The method is rapid and especially applicable to routine sample analysis for "grab" samples.

2.0 Range and Sensitivity

The lower limit of measurement for methyl chloride and methyl bromide is ∿10 ppb and ∿0.5 ppb, respectively (4). The linear dynamic range for the electron capture is ∿500 and therefore the upper limit of measurement is ∿5,000 ppb and ∿250 ppb for methyl chloride and methyl bromide, respectively using a 5 ml sampling loop.

3.0 Interferences

At the present time there are no known common pollutants in the ambient air in sufficient concentrations to interfere with the estimation of methyl chloride and methyl bromide. The chromatographic conditions selected for this analysis should resolve dichloridifluoromethane, trifluoromethane, methylene chloride, chloroform and carbon tetrachloride from methyl chloride and methyl bromide (1,2).

4.0 Precision and Accuracy

Replicate analysis of ambient air samples containing known standard methyl chloride and methyl bromide air vapor mixtures should not deviate by more than ±20% relative standard deviation using this procedure. The absolute accuracy of this procedure is approximately ±30% (2,3).

5.0 Apparatus

5.1 Chromatographic Columns

A stainless steel column (10 ft x 1/8 in o.d.) packed with Durapak *n*-octane/Poracil C (100-120 mesh) is used for effecting the separation of dichlorodifluoromethane from methyl chloride and methyl bromide. The column is housed in a Fisher Victoreen 4400 series gas chromatograph. The instrument is equipped with both pulse mode and direct current operation of the electron capture detector. The column is conditioned by passing the carrier gas through it for a minimum of 12 hrs at 20° below its upper temperature limit. During operation, the column temperature is 30°C. The carrier gas, nitrogen, is maintained at ∼10-15 ml/min. Because electron capture detection is used in this procedure, the column temperature must be isothermal throughout the entire chromatographic run (4).

5.2 Sample Injector

A six-port gas sampling valve (Valco, Houston, TX) with a 5 ml stainless steel sampling loop is used. If the concentrations of methyl chloride or methyl bromide are above the linear dynamic range of the electron capture detector, then smaller gas sampling loops may be used.

5.3 Detector

A high temperature, low volume, scandium tritide electron capture detector manufactured in this laboratory is used for this analysis (4,5). This detector was designed for low carrier gas flow rates for optimum sensitivity. The carrier gas, nitrogen, flows directly from the chromatographic column to the detector at a rate of 10-15 ml/min which is optimum for this detector. A pulse mode of 50 or 100 /sec is used during the operation of the ECD.

5.4 Electrometer

The standard vibrating reed electrometer on the Fisher Victoreen 4400 series gas chromatograph is used. This electrometer is capable of amplifying down to 10^{-13} afs.

5.5 Recorder

A Varian A-25 strip chart recorder with selectable ranges of 0-1, 0-10, 0-100, 0-1,000 and 0-5,000 millivolts and chart speeds are used. The pen response is 1 sec.

5.6 Sampling Containers

Since studies have indicated that Tedlar® bags are inadequate for sampling halocarbons because of their high permeability through teflon membranes, aluminum sample containers (Altech Assoc.) are used for sampling and storing the halocarbons samples (6). The aluminum containers (280 ml) are evacuated at the laboratory and background checks are run on the containers prior to deployment to the field. Two to three alumnimum sample containers are transported to the field containing known concentrations of methyl chloride and methyl bromide for quality control purposes. Also 2-3 containers are carried to and from the field site for determining potential contamination during transportation and storage. The containers are fitted with a gas-tight valve which allows their air evacuation with a vacuum pump at the laboratory and sealing of the container until ready for use in the field. A vacuum gauge is used in the field to check their vacuum prior to their use. The results of a one month storage test on halocarbons using these containers have indicated a 3% loss of their original concentration (6).

Since the aluminum sampling containers are under a vacuum when deployed to the field, these sampling containers are used for obtaining "grab" samples. This is simply achieved by opening the valve on the sample container until the interior and exterior atmospheric pressure reach an equilibrium. The valve is then closed which provides a permanent seal for transportation back to the laboratory where the analysis is performed.

The exact volume of the sample collected is fixed by the container at 280 ml, however this information is not necessary for the analysis during the gas chromatographic step. The concentration of methyl chloride and methyl bromide in the ambient air is based on the volume of the sampling loop (5 ml) which is employed on a six-port valve affixed to the gas chromatograph.

6.0 Materials

Methyl Chloride - Matheson, Chicago, IL.

Methyl Bromide - Matheson, Chicago, IL.

Durapak, n-octane/Poracil C (100/120 mesh) - Applied Science Lab., State College, PA.

Six-port, 2 position Valve - Valco Inst., Houston, TX.

7.0 Procedure

7.1 Collection of Field Samples

Aluminum sampling containers with a capacity of 280 ml are used to collect ambient air samples of methyl chloride and methyl bromide. The containers are equipped with a vacuum-tight valve which allows the evacuation of the container in the laboratory and filling at the sampling site. This collection procedure is for obtaining "instant grab" samples.

During collection of the samples, observations are carefully recorded with regard to the meteorological conditions surrounding the sampling area. The aluminum cannister containing the collected sample are identified with a code and recorded according to the approximate information such as date, time of sample collection, location of sample collection which corresponds to the meteorological conditions at that sampling location.

7.2 Transport and Storage

The aluminum sampling containers are impermeable to hydrocarbons and freons and thus free of external contamination. Storage experiments on samples of ambient air containing freons which are related to methyl chloride and methyl bromide have shown the samples to be relatively stable upto four weeks after collection (6). However, analysis will be performed as soon as possible after collection.

7.3 Range of Methyl Chloride and Methyl Bromide Concentrations Anticipated

The ambient air concentrations have been shown to be in some cases, about 0.5 to 5 ppm at ground level (2). The methyl bromide concentration has been observed to be considerably less. Thus, the analytical technique employed for the analysis of methyl chloride and methyl bromide surrounding the bromine industry should have sufficient sensitivity for the measurement of these compounds above background levels.

8.0 Calibration and Standards

Calibration standards for methyl chloride and methyl bromide are prepared in hydrocarbon free air or Ar. The retention time is used for identifying methyl chloride and methyl bromide and the peak areas are measured for quantification of these compounds. Standard calibration mixtures are based on a commercial source of methyl chloride and methyl bromide. Dilutions from the primary standard of methyl chloride and methyl bromide are made in the aluminum sampling containers. This is accomplished by introducing a predetermined amount of methyl chloride and methyl bromide from a permeation tube into hydrocarbon free air and the synthetic air-vapor mixture is metered into the sampling container. Based upon flow-rate of gas to the sampling container (280 ml) and the permeation rate of methyl chloride and methyl bromide tubes, the final dilution is calculated. A series of dilutions is prepared by adjusting the flow rates across the permeation tubes.

Approximately 10-15 ml of the standard gas mixture is flushed through the 5 ml stainless steel sampling loop of the six-port valve. A 5 ml sample of the standard gas mixture is then injected into the gas chromatogram.

9.0 Calculation

The concentrations of methyl chloride and methyl bromide in ambient air samples collected in the field and returned to the laboratory are calculated according to the following procedure. The response of the electron capture detector to known concentrations of methyl chloride and methyl bromide is recorded on the strip chart recorder as they are eluted fron the chromatographic column. The time of elution is recorded for each compound. Peak area is used for quantitating methyl chloride and methyl bromide and the concentration is determined in the unknown sample by using the calibration response factor: ppb, halogenated hydrocarbon = f x peak response x attenuation where f is the calibration response factor for methyl chloride or methyl bromide in units of ppb/mm^2 peak area, peak response is the peak area in mm^2 for methyl bromide and attenuation is the electrometer attenuation setting.

The response factors for methyl chloride and methyl bromide at three different concentrations are averaged. The concentration of the standard (ppb) divided by the detector response (mm^2) times the attenuation yields the response factor.

10.0 References

1. Farwell, S. O. and R. A. Rasmussen, J. Chromat. Sci., 14, 224 (1976).
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4. Pellizzari, E. D., Chromatog. Rev., 98, 323 (1974).
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6. Denyszyn, R. B., L. T. Hackworth, F. M. Groshe, and D. E. Wagoner, Inst. Conf. Photochem. Oxid. Poll. and its Control, Raleigh, NC, 1976.

Analytical Protocol revised 1/24/77.

E. SAMPLING AND ANALYSIS FOR METHYL CHLORIDE, METHYL BROMIDE, VINYL CHLORIDE AND VINYL BROMIDE IN AMBIENT AIR

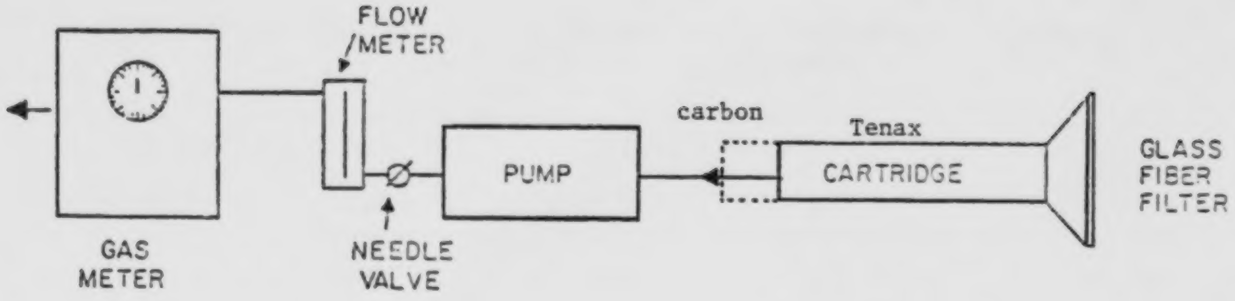
1.0 Principle of Method

Methyl chloride, methyl bromide, vinyl chloride and vinyl bromide are concentrated from ambient air on SKC carbon in a short, glass tube (1). Recovery of these volatile halogenated hydrocarbons is accomplished by thermal desorption and purging with helium to transfer the trapped vapors from the carbon cartridge to a Tenax GC cartridge through a calcium sulfate drying tube to remove excessive amounts of water. Then the vapors are recovered from Tenax by thermal desorption and purging with helium into a liquid nitrogen cooled nickel capillary trap (2) and the vapors are introduced onto a high resolution glass, gas chromatographic column where the constituents are separated from each other (2). Identification and quantification of methyl chloride, methyl bromide, vinyl chloride and vinyl bromide in the sample are accomplished by mass spectrometry either by measuring the intensity of the total ion current signal or mass fragmentography (3). The collection and analysis systems are shown in Figure E1.

2.0 Range and Sensitivity

The linear range of the mass spectrometric signals for the halogenated compounds depend upon two principle features. The first is a function of the breakthrough volume of each specific compound trapped on the SKC carbon sampling cartridge and the second is related to the inherent sensitivity of the mass spectrometry for methyl chloride, methyl bromide, vinyl chloride and vinyl bromide (3,4). Thus, the range and sensitivity is direct function of each compound. The linear range for quantification on the gas chromatograph/mass spectrometry/computer (gc/ms/comp) is generally over three orders of magnitude. Tables E1 and E2 lists the breakthrough volumes for methyl chloride, methyl bromide, vinyl chloride and vinyl bromide on SKC charcoal (104).

Table E3 lists the approximate limits of detection for methyl chloride, methyl bromide, vinyl chloride and vinyl bromide based upon these breakthrough volumes. As it might be expected, the highest sensitivity is observed for vinyl bromide, and the lowest for methyl chloride. Nevertheless, the limits of detection are in the parts per trillion range.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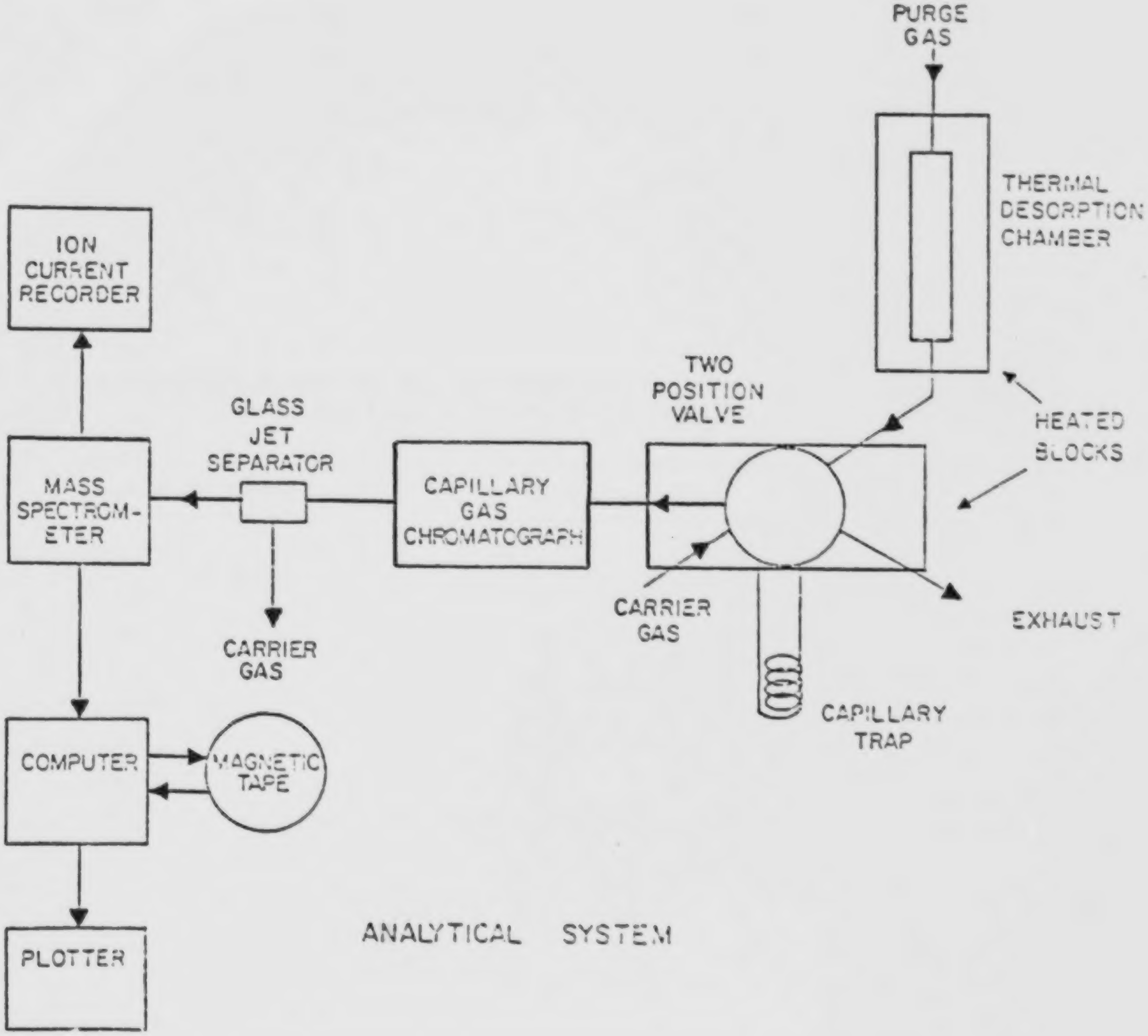
VAPOR COLLECTION SYSTEM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CARRIER
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MAGNETIC
TAPE
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ANALYTICAL SYSTEM

Figure E1. Vapor collection and analytical systems for analysis of organic vapors in ambient air.

Table E1. ESTIMATION OF BREAKTHROUGH VOLUMES FOR VINYL CHLORIDE AND VINYL BROMIDE ON SKC CHARCOAL (104)

Temperature °C (°F)	Vinyl Chloride		Vinyl Bromide	
	ℓ/g	ℓ/2.52 g[a]	ℓ/g	ℓ/2.52 g[a]
10 (50)	104	262	388	978
15.5 (60)	81	204	306	771
21.1 (70)	63	159	241	608
26.7 (80)	49	123	190	479
32.2 (90)	38	96	150	378
37.8 (100)	30	76	118	298

[a] A 1.5 cm i.d. x 4.0 cm bed of charcoal weighs 2.52. g.

Table E2. ESTIMATION OF BREAKTHROUGH VOLUMES FOR METHYL CHLORIDE AND METHYL BROMIDE ON SKC CHARCOAL (104)

Temperature °C (°F)	Methyl Chloride		Methyl Bromide	
	ℓ/g	ℓ/2.52 g	ℓ/g	ℓ/2.52 g
10 (50)	14.3	36	98	248
15.5 (60)	11.1	28	75	188
21.1 (70)	8.7	22	57	143
26.7 (80)	7.5	19	43	108
32.2 (90)	5.6	14	32	82
37.8 (100)	4.4	11	25	62

Table E3. APPROXIMATE LIMIT OF DETECTION FOR METHYL CHLORIDE, METHYL BROMIDE, VINYL CHLORIDE AND VINYL BROMIDE[a]

	Ambient Air Temperature °C (°R)				
	10 (50)	15.5 (60)	21.1 (70)	26.7 (132)	32.2 (90)
Methyl chloride[b]	138 (69)	178 (89)	227 (114)	253 (132)	357 (178)
Methyl bromide[b]	8 (2.1)	11 (2.8)	14 (3.6)	18 (4.8)	24 (6.3)
Vinyl chloride[c]	48 (20)	62 (26)	79 (33)	102 (42)	131 (55)
Vinyl bromide[c]	5 (1.2)	6.5 (1.5)	8.2 (1.9)	10.5 (2.5)	28 (6.7)

[a] Values are in ng/m^3 (ppt)

[b] Estimation of L.O.D. based on 2.52 g carbon.

[c] Estimation of L.O.D. based on 1.0 g carbon.

3.0 Interferences

Because of the unique isotopic clusters for chlorine and bromine in these compounds the background that is generally observed at their retention times on a glass capillary column will not interfer with their qualitative and quantitative analyses.

4.0 Reproducibility

The reproducibility of this method has been determined to be approximately ±20% of the relative standard deviation for the four compounds when replicate sampling are examined (3). The reproducibility is a function of several factors. (1) The ability to acurately determine the breakthrough volume for each compound; (2) The accurate measurement of the ambient air volume sampled; (3) The percent recovery of the halogenated hydrocarbon from the sampling carbon cartridge after a period of storage; (4) The reproducibility of thermally recovering each compound from the carbon cartridge and of sample introduction into the analytical system; (5) The accuracy and determination of the relative molar response ratios between the methyl chloride, methyl bromide, vinyl chloride and vinyl bromide and the external standards used for calibrating the analytical system; (6) The relative efficiency and reproducibility of transferring the trapped vapors from the carbon sampling cartridge to the Tenax GC cartridge prior to analysis in order to remove the excessive amounts of water using calcium chloride; (7) The reproducibility of transmitting the sample through the high resolution gas chromatographic column, and (8) The day-to-day reliability of the ms/comp system (2-4).

The accuracy of analysis is generally ±15% of the amount determined from repeated analysis of the authentic halogenated hydrocarbons. The accuracy of the analysis is dependent upon the storage period.

5.0 Apparatus

5.1 Sampling Cartridges

The sampling tubes are prepared by packing a 10 cm long x 1.5 cm id glass tube containing two or four cm of SKC carbon Lot No. 104 with glass wools in the ends to provide support (3,4). The carbon cartridges are conditioned at 400°C with a helium flow of approximately 30 ml/min for 30 min. The conditioned cartridges are transferred to Kimax® culture tubes immediately sealed using Teflon lined caps and cooled. This procedure is performed in order to avoid recontamination of the sorbent bed (3,4).

Cartridge samplers with longer beds of sorbents may be prepared using a proportional increased amount of carbon in order to achieve a larger breakthrough volume for each compound and thus increasing the overall sensitivity of the technique. However, it must be noted that the percent recovery of the halogenated hydrocarbon significantly decreases when the amount of carbon is increased and/or when an excessive length of storage period is employed (more than a week).

5.2 Gas Chromatographic Column

A 0.35 mm i.d. x 100 m glass SCOT capillary column coated with OV-101 stationary phase and 0.1% benzyltriphenylphosphonium chloride is used for effecting the resolution of the four halogenated hydrocarbons. The capillary column is conditioned for 48 hrs at 230°C at 1.5 - 2.0 ml/min of helium flow.

A Finnigan type glass type jet separator on a Varian MAT CH-7 gc/ms/comp system is employed to interface the glass capillary column to the mass spectrometer. The glass jet separator is maintained at 240°C.

5.3 Inlet-Manifold

An inlet-manifold for thermally recovering methyl chloride, methyl bromide, vinyl chloride and vinyl bromide trapped on SKC carbon sampling cartridges is employed and is shown in Figure E1 (1-3).

5.4 Gas Chromatograph

A Varian 1700 gas chromatograph is used to house the glass capillary column and is interfaced to the inlet-manifold (Figure E1).

5.5 Mass Spectrometry/Computer

A Varian MAT CH-7 mass spectrometer with a resolution of 2000 equipped with single ion monitoring and mass fragmentography capabilities is used in tandem with the gas chromatograph (Figure E1). The mass spectrometer is interfaced to Varian 620/1 computer (Figure E1).

6.0 Reagents and Materials

SKC carbon Lot No. 104 is from SKC Carbon Company, Boston, MA. All reagents used are analytical reagent grade and distilled in glass prior to use.

7.0 Procedure

7.1 Cleaning of Glassware

All glassware, sampling tubes, cartridge holders, etc. are washed in Isoclean®/water, rinsed with deionized distilled water, acetone and air dried. Glassware is heated to 450-500°C for two hours to insure that all organic material has been removed prior to its use.

7.2 Preparation of Carbon

Virgin carbon is packed into glass sampling tubes without further purification. Used carbon cartridges are not recycled.

7.3 Collection of Methyl Chloride, Methyl Bromide, Vinyl Chloride and Vinyl Bromide in Ambient Air

Continuous sampling of ambient air is accomplished using a Nutech Model 221-A portable sampler (Nutech Corp., Durham, NC, see Figure E1). Flow rates are maintained at 1 ℓ/min using critical orifaces and the total flow is monitored through a calibrated rotameter. The total flow is also registered by a dry gas meter. Concomitant with these parameters the temperature is continuously recorded with a Meteorology Research Incorporated weather station since the breakthrough volume is important in order to obtain quantitative data on these four halogenated hydrocarbons. This portable sampling unit operates on a 12-volt storage battery and it is capable of continuous operation up to a period of 24 hours. However, in most cases at the rates which will be employed in the field. The sampling period will consist of one to two hours. This portable sampling unit is utilized for obtaining "high volume" samples. Duplicate cartridges are deployed on each sampling unit and are in tandem with Tenax GC cartridges. The carbon cartridges serve as a backup to the Tenax GC cartridge for collecting the more highly volatile constituents such as these four halogenated hydrocarbons which have a low breakthrough volume on Tenax GC. A total of four portable sampling units are available for sampling ambient air surrounding the bromine industry.

In addition to the Nutech samplers, five DuPont personal samplers are used to sample "low volumes" ambient air as well as long term integrated samples (12-36 hrs). An identical SKC carbon sampling cartridge is employed in this case and sampling is conducted in duplicate. The flow rate is balanced between duplicate cartridges using critical orifices to maintain a rate of 25 or 100 ml/min per cartridge.

7.4 Analysis of Sample

The conditions for transferring methyl chloride, methyl bromide, vinyl chloride and vinyl bromide from SKC carbon sampling cartridges to Tenax GC sampling cartridges prior to instrumental analysis is shown in Table E4. A 1.5 x 2 cm bed of calcium sulfate is used to remove the water vapor prior to retrapping the halogenated hydrocarbon vapors onto the Tenax GC sampling cartridge.

The instrumental conditions for the analysis of the four halogenated hydrocarbons on the sorbent carbon sampling cartridge is shown in Table E5.

7.4.1 Operation of the MS/Comp System (Figure E1)

The operation of the ms/comp system is identical to as that described for the Analytical Protocol under Section F entitled, "Sampling and Analysis for Chlorinated and Brominated Hydrocarbons in Ambient Air".

7.4.2 Quantitative Analysis

The procedure for the estimation of the level of methyl chloride, methyl bromide, vinyl chloride and vinyl bromide by capillary gas chromatography in combination with mass spectrometry is identical to that described for the analytical protocol F entitled, "Sampling and Analysis for Chlorinated and Brominated Hydrocarbons in Ambient Air".

8.0 References

1. Pellizzari, E. D. Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres. EPA Contract No. 68-02-1228, EPA-650/2-74-121, July 1974, 148 pp.
2. Pellizzari, E. D. Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. EPA Contract No. 68-02-1228, EPA-600/2-75-076, November 1975, 187 pp.
3. Pellizzari, E. D. Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. EPA Contract No. 68-02-1228, 1976, in preparation.
4. Pellizzari, E. D. Identification of Atmospheric Pollutants by the Combined Techniques of Gas Chromatography/Mass Spectrometry. EPA Contract No. 68-02-2262, 1976, in preparation.

Analytical protocol revised 1/31/77.

Table E4. PARAMETERS FOR REMOVING WATER AND TRANSFERRING VAPORS TO TENAX GC

Parameters	Condition
Inlet-manifold	
desorption chamber	295°C
valve	200°C
$CaSO_4$ drying tube (1.5 x 2.0 cm)	ambient temperature
transfer line	ambient temperature
Tenax GC cartridge (1.5 x 6.0 cm)	ambient temperature
Desorption time	10 minutes
He purge rate	10 ml/min

Table E5. OPERATING PARAMETERS FOR GLC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	270°C
valve	220°C
capillary trap - minimum	-195°C
maximum	+180°C
thermal desorption time	4 min
GLC	
100 m glass SCOT-OV-101	20-240°C, 4/C°C min
carrier (He) flow	∿3 ml/min
transfer line to ms	240°C
MS	
scan range	*m/e* 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	6.0
ion source vacuum	∿4 x 10^{-6} torr

F. SAMPLING AND ANALYSIS FOR CHLORINATED AND BROMINATED HYDROCARBONS AND OTHER CHEMICALS IN AMBIENT AIR

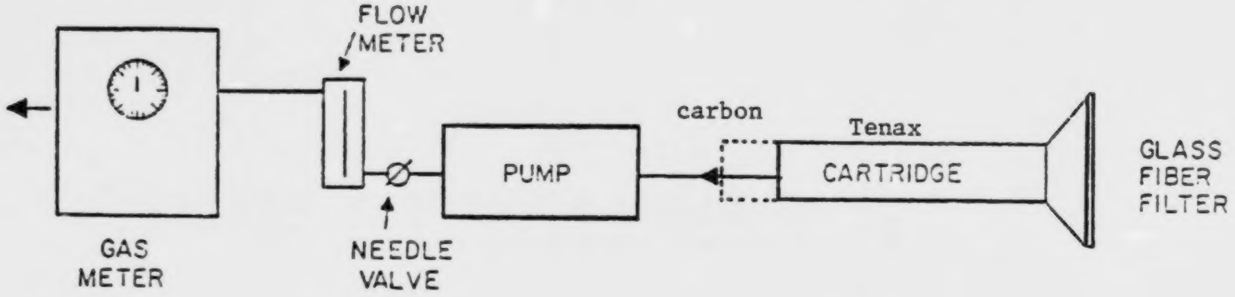
1.0 Principle of Method

Chlorinated and brominated hydrocarbons are concentrated from ambient air on Tenax GC in a short glass tube (1-3). Recovery of the halogenated hydrocarbons is accomplished by thermal desorption and purging with helium into a liquid nitrogen cooled nickel capillary trap (1,2,4) and then vapors are introduced onto a high resolution glass gas chromatographic column where the constituents are separated from each other (2,5). Characterization and quantitation of the constituents in the sample are accomplished by mass spectrometry, either by measuring the intensity of the total ion current signal or mass fragmentography (2,6). The collection and analysis systems are shown in Figure F1.

2.0 Range and Sensitivity

The linear range of the mass spectrometric signals for the halogenated compounds depends upon two principal features. The first is a function of the breakthrough volume of each specific compound trapped on the Tenax GC sampling cartridge, and the second is related to the inherent sensitivity of the mass spectrometer for each halogenated hydrocarbon and other organics (2,7). Thus, the range and sensitivity is a direct function of each compound which is identified. The linear range for quantitation on the gas chromatograph/mass spectrometer/computer (gc-ms-comp) is generally three orders of magnitude. Table F1 lists the overall theoretical sensitivity for some examples of halogenated hydrocarbons as well as other chemicals which is based on these two principles (7).

The sensitivity of this technique for the organic compounds vinyl chloride, vinyl bromide, methyl chloride, methyl bromide and ethylene is inadequate for the purpose of this study. Alternate methods are suggested. Tris-(2,3-dibromopropyl)phosphate and decabromobiphenyl ether cannot be analyzed by this procedure. Bromobutyric acid has not been tested and therefore its behavior is unknown. We believe that the following compounds which are listed as emissions by the industry can be adequately analyzed: benzol, carbon tetrachloride, diphenyl, epibrom, epichlor, ethylene dibromide, hexane, bromobenzene, dibromopropanol, allyl alcohol, phenol, glycol,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VAPOR COLLECTION SYSTEM

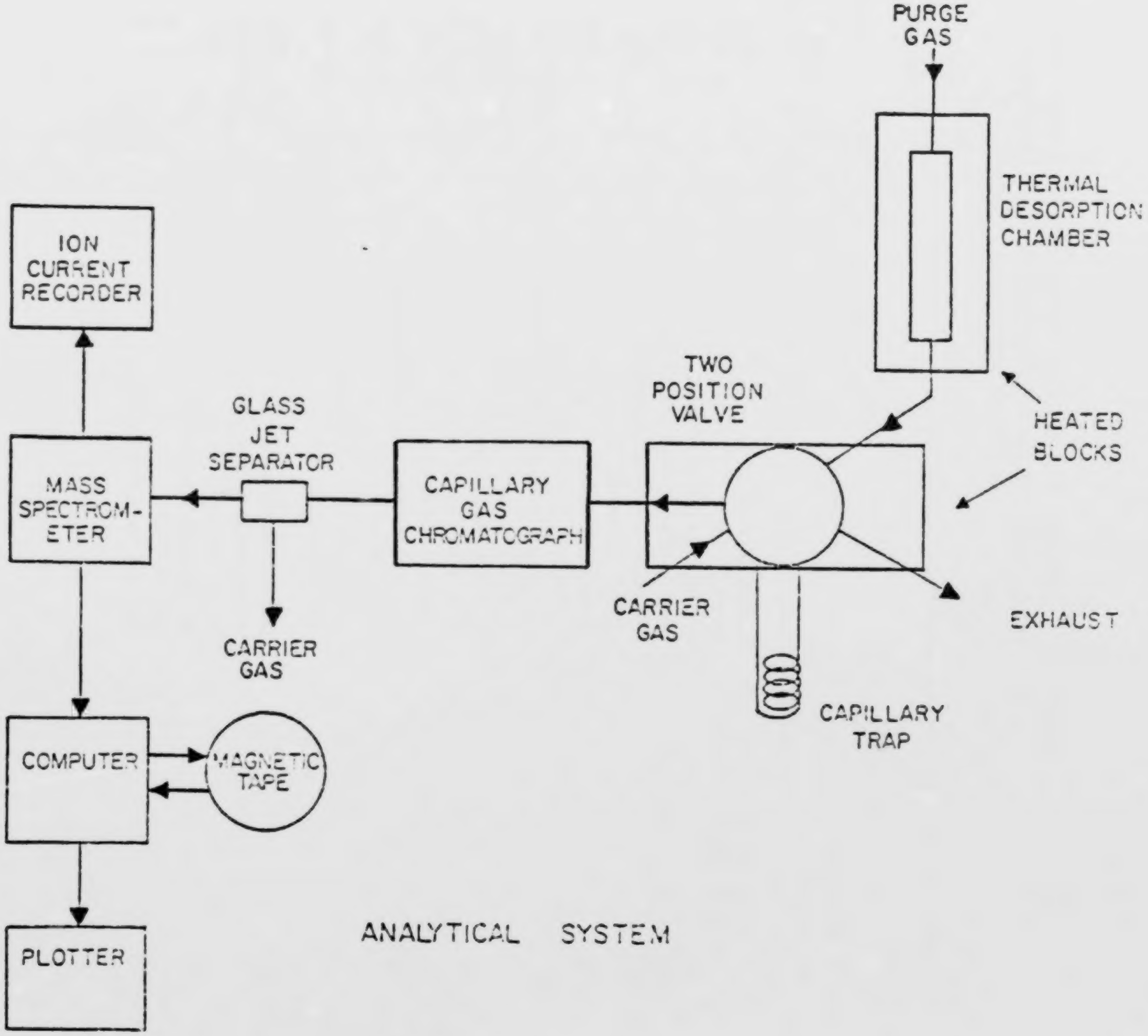
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Figure F1. Vapor collection and analytical systems for analysis of organic vapors in ambient air.

Table F1. OVERALL THEORETICAL SENSITIVITY OF HIGH RESOLUTION GAS CHROMATOGRAPHY/MASS SPECTROMETRY/COMPUTER ANALYSIS FOR ATMOSPHERIC POLLUTANTS

Chemical Class		Estimated Detection Limit[a]	
		ng/m^3	ppt
Halogenated hydrocarbon	Vinyl bromide	250	57
	Bromoform	0.340	0.03
	Bromodichloromethane	1.300	0.22
	Dibromochloromethane	0.667	0.07
	1-Bromo-2-chloroethane	1.00	0.67
	Allyl bromide	5.00	1.04
	1-Bromopropane	5.200	1.06
	1-Chloro-3-bromopropane	0.150	0.01
	1-Chloro-2,3-dibromopropane	~0.100	<0.01
	1,1-Dibromo-2-chloropropane	~0.100	<0.01
	1,2-Dibromoethane	0.530	0.07
	1,3-Dibromopropane	~0.100	~0.01
	Epichlorohydrin (1-Chloro-2,3-epoxypropane)	9.600	2.50
	Epibromohydrin (1-Bromo-2,3-epoxypropane)	0.300	0.05
	Bromobenzene	0.100	0.02
	Methyl bromide	500	135
	Methyl chloride	2000	1000
	Vinyl chloride	800	333
	Methylene chloride	700	200
	Chloroform	200	420
	Carbon tetrachloride	250	400

Table F1 (cont'd)

Chemical Class	Compound	Estimated Detection Limit[a]	
		ng/m^3	ppt
Halogenated hydrocarbon (cont'd)	1,2-Dichloroethane	32	8.15
	1,1,1-Trichloroethane	66	12.45
	Tetrachloroethylene	2.5	0.38
	Trichloroethylene	10	1.92
	1-Chloro-2-methylpropene	62	21.5
	3-Chloro-2-methylpropene	62	21.5
	3-Chloro-1-butene	83	28.8
	Allyl chloride	83	28.8
	4-Chloro-1-butene	38	13.2
	1-Chloro-2-butene	13	4.5
	Chlorobenzene	2.10	0.47
	o-Dichlorobenzene	1.00	0.06
	m-Dichlorobenzene	0.75	0.01
	Benzylchloride	0.65	0.01
Halogenated ethers	2-Chloroethyl ethyl ether	4.15	0.97
	Bis-(chloromethyl)ether	1.0	1.10
Nitrosamines	N-Nitrosodimethylamine	5.0	1.67
	N-Nitrosodiethylamine	3.0	0.74
Oxygenated	Acrolein	~100	56.5
	Glycidaldehyde	~59	19.5
	Propylene oxide	~60	25.5
	Butadiene diepoxide	~20	6.7

Table F1 (cont'd)

Chemical Class	Compound	Estimated Detection Limit[a]	
		ng/m^3	ppt
Oxygenated hydrocarbons (continued)	Cyclohexene oxide	~10	2.5
	Styrene oxide	2	0.415
	Acetophenone	~2	~0.415
	β-Propiolactone	~3	~1.2
Nitrogenous Compounds	Nitromethane	8	~2.4
	Aniline	3.0	0.78
Sulfur Compounds	Diethyl sulfate	~50	-
	Ethyl methane sulfate	~5.0	-

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[a] Limits are calculated on the basis of the breakthrough volume for 2.2 g of Tenax GC, capillary column performance and sensitivity of the mass spectrometer to that compound in the mass fragmentography mode of most intense ion.

aliphatic alcohols (> C_4), tribromoethane, bromophenol, brominated aromatic ethers (<3Br), fumazone, trimethylene chlorobromide, allyl chloride, 1,2-chlorobromopropane, dichloropropane, isopropyl chloride and chlorobutyronitrile. Many other halogenated hydrocarbons and aromatics can potentially be assayed if present in ambient air.

3.0 Interferences

Because of the unique isotopic clusters for chlorine and bromine in the hydrocarbons, the hydrocarbon background generally observed occurring from either auto exhaust or the petroleum industry will not interfere with qualitative and quantitative analyses. The potential difficulties with this technique are primarily associated with those cases where isomeric forms of a particular halogenated substance cannot be resolved by the high resolution chromatographic column and the mass cracking pattern of each of the isomers are identical. Since the complete composition of ambient air surrounding the bromine industry is not known dismissal of possible interferences cannot be unequivocally stated.

4.0 Reproducibility

The reproducibility of this method has been determined to range from ±10 to ±30 percent of the relative standard deviation for different substances when replicate sampling cartridges are examined (5). The reproducibility is a function of several factors: (1) the ability to accurately determine the breakthrough volume for each of the identified halogenated compounds, (2) the accurate measurement of the ambient air volume sampled, (3) the percent recovery of the halogenated hydrocarbon from the sampling cartridge after a period of storage, (4) the reproducibility of thermally recovering a compound from the cartridge and of sample introduction into the analytical system, (5) the accuracy in the determination of the relative molar response ratios between the identified halogenated substance and the external standard used for calibrating the analytical system, (6) the reproducibility of transmitting the sample through the high resolution glass chromatographic column, and (7) the day-to-day reliability of the ms-comp system (1-8).

The accuracy of the analysis is generally ±20 percent of the amount determined from repeated analyses of the authentic halogenated hydrocarbon. However, the accuracy of analysis is dependent upon the chemical and physical nature of the compound (2,8).

5.0 Advantages and Disadvantages of the Method

The gas chromatograph-mass spectrometer interfaced with a Finnigan glass jet separator is extremely sensitive and specific for the analysis of halogenated hydrocarbons. The high resolution gas chromatographic separation provides adequate resolution of the halogenated hydrocarbons for their subsequent quantification. The combination of the high resolution gas chromatographic column and the selection of specific or unique ions representing the various halogenated hydrocarbons identified in air samples yields a relatively specific assay method for these compounds (1-8).

Collected samples can be stored up to one month with less than 10 percent losses (2,8). Because some of the halogenated hydrocarbons could be hazardous to man, it is extremely important to exercise safety precautions in the preparation and disposal of liquid and gas standards, cleaning of used glassware, etc. and the analysis of air samples.

Since the mass spectrometer cannot be conveniently mobilized, sampling must be carried out away from the instrument.

The efficiency of air sampling increases as the ambient air temperature decreases (that is, sensitivity increases) (8).

The retention of water by Tenax is low, its thermal stability is high and its background is negligible allowing sensitive analysis (1,2,5,8).

6.0 Apparatus

6.1 Sampling Cartridges

The sampling tubes are prepared by packing a 10 cm long x 1.5 cm i.d. glass tube containing 6.0 cm of 35/60 mesh Tenax GC with glass wool in the ends to provide support (2,5). Virgin Tenax is extracted in a Soxhlet extractor for a minimum of 18 hours with acetone prior to preparation of cartridge samplers (2,5). After purification of the Tenax GC sorbent and drying in a vacuum oven at 100°C for 2-3 hr all the sorbent material is meshed to provide a 35/60 particle size range. Cartridge samplers are then prepared and conditioned at 270°C with helium flow at 30 ml/min for 30 minutes. The conditioned cartridges are transferred to Kimax® (2.5 cm x 150 cm) culture tubes, immediately sealed using Teflon lined caps, and cooled. This procedure is performed in order to avoid recontamination of the sorbent bed (2,5).

Cartridge samplers with longer beds of sorbent may be prepared using a proportional increased amount of Tenax in order to achieve a larger breakthrough volume for each compound and thus increasing the overall sensitivity of the technique (8).

6.2 Gas Chromatographic Column

A 0.35 mm i.d. x 100 m glass SCOT capillary column coated with OV-101 stationary phase and 0.1% benzyl triphenylphosphonium chloride is used for effecting the resolution of the halogenated hydrocarbons and other chemicals (5). The capillary column is conditioned for 48 hours at 230°C at 1.5-2.0 ml/min of helium flow. For highly polar pollutants of interest an 80 m carbowax 20 M glass SCOT capillary is used.

A Finnigan type glass jet separator on a Varian-MAT CH-7 gc/ms/comp system is employed to interface the glass capillary column to the mass spectrometer. The glass jet separator is maintained at 240°C (2.5).

6.3 Inlet Manifold

An inlet manifold for thermally recovering vapors trapped on Tenax sampling cartridges is employed and is shown in Figure F1 (1,2,4,5)

6.4 Gas Chromatograph

A Varian 1700 gas chromatograph is used to house the glass capillary column and is interfaced to the inlet manifold (Fig. F1).

6.5 Mass Spectrometry/Computer

A Varian-MAT CH-7 mass spectrometer with a resolution of 2,000 equipped with a single ion monitoring capabilities is used in tandem with the gas chromatograph (Fig. F1). The mass spectrometer is interfaced to a Varian 620L computer (Fig. F1).

7.0 Reagents and Materials

All reagents used are analytical reagent grade.

8.0 Procedure

8.1 Cleaning of Glassware

All glassware, sampling tubes, cartridge holders, etc. are washed in Isoclean®/water rinsed with deionized-distilled water, acetone and air dried. Glassware is heated to 450-500°C for 2 hours to insure that all organic material has been removed prior to its use.

8.2 Preparation of Tenax GC

Virgin Tenax GC is extracted in a Soxhlet apparatus for a minimum of 18 hours with acetone prior to its use. The Tenax GC sorbent is dried in a vacuum oven at 100°C for 2-3 hr and then sieved to provide a fraction corresponding to 35/60 mesh. This fraction is used for preparing sampling cartridges. In those cases where sampling cartridges of Tenax GC are recycled, the sorbent is extracted in a Soxhlet apparatus with acetone as described for the Virgin material, but the sorbent is further extracted with a non-polar solvent, hexane, in order to remove the relatively non-polar and non-volatile materials which might have accumulated on the sorbent bed during previous sampling periods.

8.3 Collection of Halogenated Hydrocarbons in Ambient Air

Continuous sampling of ambient air is accomplished using a Nutech Model 221-A portable sampler (Nutech Corp., Durham, NC, see Fig. Fl, ref. 2). Flow rates are maintained at 1 ℓ/min using critical orifices, and the total flow is monitored through a calibrated rotameter. The total flow is also registered by a dry gas meter. Concomitant with these parameters, the temperature is continuously recorded with a Meterology Research Incorp. weather station since the breakthrough volume is important in order to obtain quantitative data on the halogenated hydrocarbons. This portable sampling unit operates on a 12 volt storage battery and is capable of continuous operation up to a period of 24 hours. However, in most cases at the rates which will be employed in the field, the sampling period will consist of 1 to 2 hours. This portable sampling unit will be utilized for obtaining "high volume" samples. Duplicate cartridges are deployed on each sampling unit. A total of four portable sampling units are available for sampling ambient air surrounding the bromine industry. In addition to the Nutech samplers five DuPont personnel samplers are used to sample "low volumes" of ambient air as well as long term integrated samples (12-36 hours). The identical Tenax GC sampling cartridge is employed in this case and sampling is conducted in duplicate. The flow rate is balanced between duplicate cartridges using critical orifices to maintain a rate of 25 or 100 ml/min/cartridge.

For large sample volumes it is important to realize that a total volume of air may cause elution of halogenated hydrocarbons through the sampling tube if their breakthrough volume is exceeded. The breakthrough volumes of some halogenated hydrocarbons are shown in Table F2 (2,4,7,8). These breakthrough volumes have been determined by a previously described technique (2). The breakthrough volume is defined as that point at which 50% of a discrete sample introduced into the cartridge is lost. Although the identity of a compound during ambient air sampling is not known (therefore also its breakthrough volume) the compound can still be quantified after identification by gc/ms/comp once the breakthrough volume has subsequently established. Thus the last portion of the sampling period is selected which represents the volume of air sampled prior to breakthrough for calculating their concentration. For cases when the identity of the halogenated hydrocarbon is not known until after glc-ms the breakthrough volume is subsequently determined.

Previous experiments have shown that organic vapors collected on Tenax GC sorbent are stable and can be quantitatively recovered from the cartridge samplers up to four weeks when they are tightly closed in cartridge holders, protected from light, and stored at 0°C (1,2).

8.4 Analysis of Sample

The instrumental conditions for the analysis of halogenated hydrocarbons of the sorbent Tenax GC sampling cartridge is shown in Table F3. The thermal desorption chamber and six-port valve are maintained at 270° and 200°C, respectively. The glass jet separator is maintained at 240°. The mass spectrometer is set to scan the mass range from 25-350. The helium purged gas through the desorption chamber is adjusted to 15-20 ml/min. The nickel capillary trap at the inlet manifold is cooled with liquid nitrogen. In a typical thermal desorption cycle a sampling cartridge is placed in the preheated desorption chamber and helium gas is channeled through the cartridge to purge the vapors into the liquid nitroged cooled nickel capillary trap [the inert activity of the trap has been shown in

Table F2. BREAKTHROUGH VOLUMES FOR SEVERAL ATMOSPHERIC POLLUTANTS[1]

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
halogenated hydrocarbon	methyl chloride	-24	0.8	0.6	0.5	0.4	0.3	0.25
	methyl bromide	3.5	3	2	2	1	1	0.9
	vinyl chloride	13	2	1.5	1.25	1.0	0.8	0.6
	methylene chloride	41	11	9	7	5	4	3
	chloroform	61	42	31	24	18	13	10
	carbon tetrachloride	77	34	27	21	16	13	10
	1,2-dichloroethane	83	53	41	31	23	18	14
	1,1,1-trichloroethane	75	23	18	15	12	9	7
	tetrachloroethylene	121	361	267	196	144	106	78
	trichloroethylene	87	90	67	50	38	28	21
	1-chloro-2-methylpropene	68	26	20	16	12	9	7
	3-chloro-2-methylpropene	72	29	22	17	13	10	8
	1,2-dichloropropane	95	229	162	115	81	58	41
	1,3-dichloropropane	121	348	253	184	134	97	70
	epichlorohydrin (1-chloro-2,3-epoxypropane)	116	200	144	104	74	54	39
	3-chloro-1-butene	64	19	15	12	9	7	6
	allyl chloride	45	21	16	12	9	6	5
	4-chloro-1-butene	75	47	36	27	20	15	12
	1-chloro-2-butene	84	146	106	77	56	40	29
	chlorobenzene	132	899	653	473	344	249	181
	o-dichlorobenzene	181	1,531	1,153	867	656	494	372
	m-dichlorobenzene	173	2,393	1,758	1,291	948	697	510
	benzyl chloride	179	2,792	2,061	1,520	1,125	830	612
	bromoform	149	507	386	294	224	171	130
	ethylene dibromide	131	348	255	188	138	101	74
	bromobenzene	155	2,144	1,521	1,079	764	542	384

Table F2 (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F) 50	60	70	80	90	100
halogenated ethers	2-chloroethyl ethyl ether	108	468	336	241	234	124	89
	Bis-(chloromethyl)ether	-	995	674	456	309	209	142
nitrosamines	N-nitrosodimethylamine	151	385	280	204	163	148	107
	N-nitrosodiethylamine	177	2,529	1,836	1,330	966	700	508
Oxygenated hydrocarbons	acrolein	53	19	14	10	8	6	4
	glycidaldehyde	-	364	247	168	114	77	52
	propylene oxide	34	35	24	17	11	8	5
	butadiene diepoxide	-	1,426	1,009	714	506	358	253
	cyclohexene oxide	132	2,339	1,644	1,153	811	570	400
	styrene oxide	194	5,370	3,926	2,870	2,094	1,531	1,119
	phenol	183	2,071	1,490	1,072	769	554	398
	acetophenone	202	3,191	2,382	1,778	1,327	991	740
	β-propiolactone	57	721	514	366	261	186	132
nitrogenous hydrocarbons	nitromethane	101	45	34	25	19	14	11
	aniline	184	3,864	2,831	2,075	1,520	1,114	817
sulfur compounds	diethyl sulfate	208	40	29	21	15	11	8
	ethyl methane sulfate	86	5,093	3,681	2,564	1,914	1,384	998
amines	dimethylamine	7.4	9	6	4	3	2	1
	isobutylamine	69	71	47	34	23	16	11
	t-butylamine	89	6	5	4	3	2	1
	di-(n-butyl)amine	159	9,506	7,096	4,775	3,105	2,168	1,462
	pyridine	115	378	267	189	134	95	67
	aniline	184	8,128	5,559	3,793	2,588	1,766	1,205
ethers	diethyl ether	34.6	29	21	15	11	8	5
	propylene oxide	35	13	9	7	5	4	3

Table F2 (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F) 50	60	70	80	90	100
esters	ethyl acetate	77	162	108	72	48	32	22
	methyl acrylate	80	164	111	75	50	34	23
	methyl methacrylate	100	736	484	318	209	137	90
ketones	acetone	56	25	17	12	8	6	4
	methyl ethyl ketone	80-2	82	57	39	27	19	13
	methyl vinyl ketone	81	84	58	40	28	19	14
	acetophenone	202	5,346	3,855	2,767	2,000	1,439	1,037
aldehydes	acetaldehyde	20	3	2	2	1	0.9	0.7
	benzaldehyde	179	7,586	5,152	3,507	2,382	1,622	1,101
alcohols	methanol	64.7	1	1	0.8	0.6	0.4	0.3
	n-propanol	97.4	27	20	14	10	7	5
	allyl alcohol	97	32	23	16	11	8	6
aromatics	benzene	80.1	108	77	54	38	27	19
	toluene	110.6	494	348	245	173	122	86
	ethylbenzene	136.2	1,393	984	693	487	344	243
	cumene	152.4	3,076	2,163	1,525	1,067	750	527
hydrocarbons	*n*-hexane	68.7	32	23	17	12	9	6
	n-heptane	98.4	143	104	75	55	39	29
	1-hexene	63.5	28	20	15	11	8	6
	1-heptene	93.6	286	196	135	93	64	44
	2,2-dimethylbutane	49.7	0.5	0.4	0.3	0.2	0.2	0.1
	2,4-dimethylpentane	80.5	435	252	146	84	49	28
	4-methyl-1-pentene	53.8	14	10	8	6	4	3
	cyclohexane	80.7	49	36	26	19	14	10

Table F2 (cont'd)

Chemical Class	Compound	b.p. (°C)	Temperature (°F)					
			50	60	70	80	90	100
inorganic gases	nitric oxide	-	0	0	0	0	0	0
	nitrogen dioxide	-	0	0	0	0	0	0
	chlorine	-	0	0	0	0	0	0
	sulfur dioxide	-	0.06	0.05	0.03	0.02	0.02	0.01
	water	100	0.06	0.05	0.04	0.03	0.01	0

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[1] Breakthrough volume is given in ℓ/2.2 g Tenax GC used in sampling cartridges.

Table F3. OPERATING PARAMETERS FOR GLC-MS-COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	270°C
valve	220°C
capillary trap - minimum	-195°C
maximum	+180°C
thermal desorption time	4 min
GLC 100 m glass SCOT-OV101	
50 m glass SCOT-Carbowax 20M	20-240°C, 4/C° min
	80-240°C
carrier (He) flow	~3 ml/min
transfer line to ms	240°C
MS	
scan range	*m/e* 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 μA
multiplier	6.0
ion source vacuum	~4 x 10^{-6} torr

previous studies (5)]. After desorption the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 10°/min); the carrier gas then introduces the vapors onto the high resolution glc column. The glass capillary column is temperature programmed from 20° to 240°C at 4°/min and held at the upper limit for a minimum of 10 min. After all of the components have eluted from the capillary column the analytical column is then cooled to ambient temperature and the next sample is processed (2).

An example of the analysis of volatile organics in ambient air is shown in Figure F2 and the background from a blank cartridge in Figure F3. The high resolution glass capillary column was coated with OV-101 stationary phase which is capable of resolving a multitude of compounds, including halogenated hydrocarbons, to allow their subsequent identification by ms-comp techniques; in this case over 120 compounds were identified in this chromatogram.

8.4.1 Operation of the MS-COMP System (Fig. F4)

Typically the mass spectrometer is first set to operate in the repetitive scanning mode. In this mode the magnet is automatically scanned exponentially upward from a preset low mass to a high mass value. Although the scan range may be varied depending on the particular sample, typically the range is set from m/e 25 to m/e 300. The scan is completed in approximately 3 seconds. At this time the instrument automatically resets itself to the low mass position in preparation for the next scan, and the information is accumulated by an on-line 620/L computer and written onto magnetic tapes or the dual disk system. The reset period requires approximately 3 seconds. Thus, a continuous scan cycle of 6 seconds/scan is maintained and repetitively executed throughout the chromatographic run. The result is the accumulation of a continuous series of mass spectra throughout the chromatographic run in sequential fashion.

Prior to running unknown samples the system is calibrated by introducing a standard substance, perfluorokerosene, into the instrument and determining the time of appearance of the known standard peaks in relation to the scanning magnetic field. The calibration curve which is thus

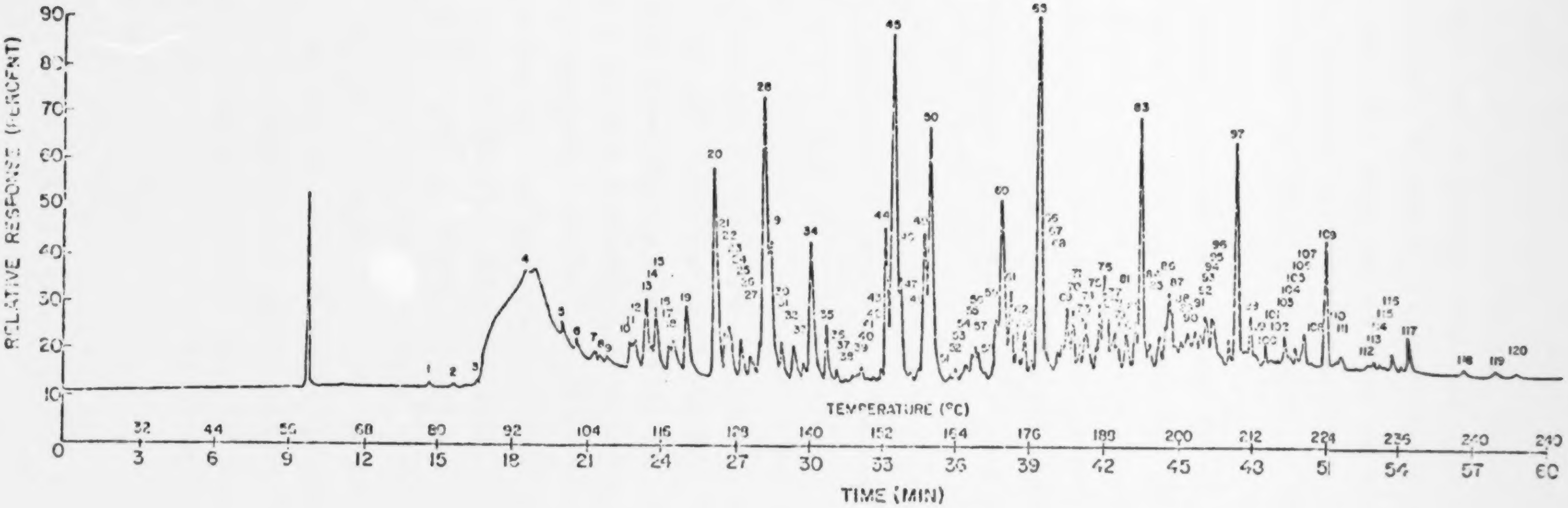

Figure F2. Profile of ambient air pollutants for Wood River, IL using high resolution gas chromatography/mass spectrometry/computer.

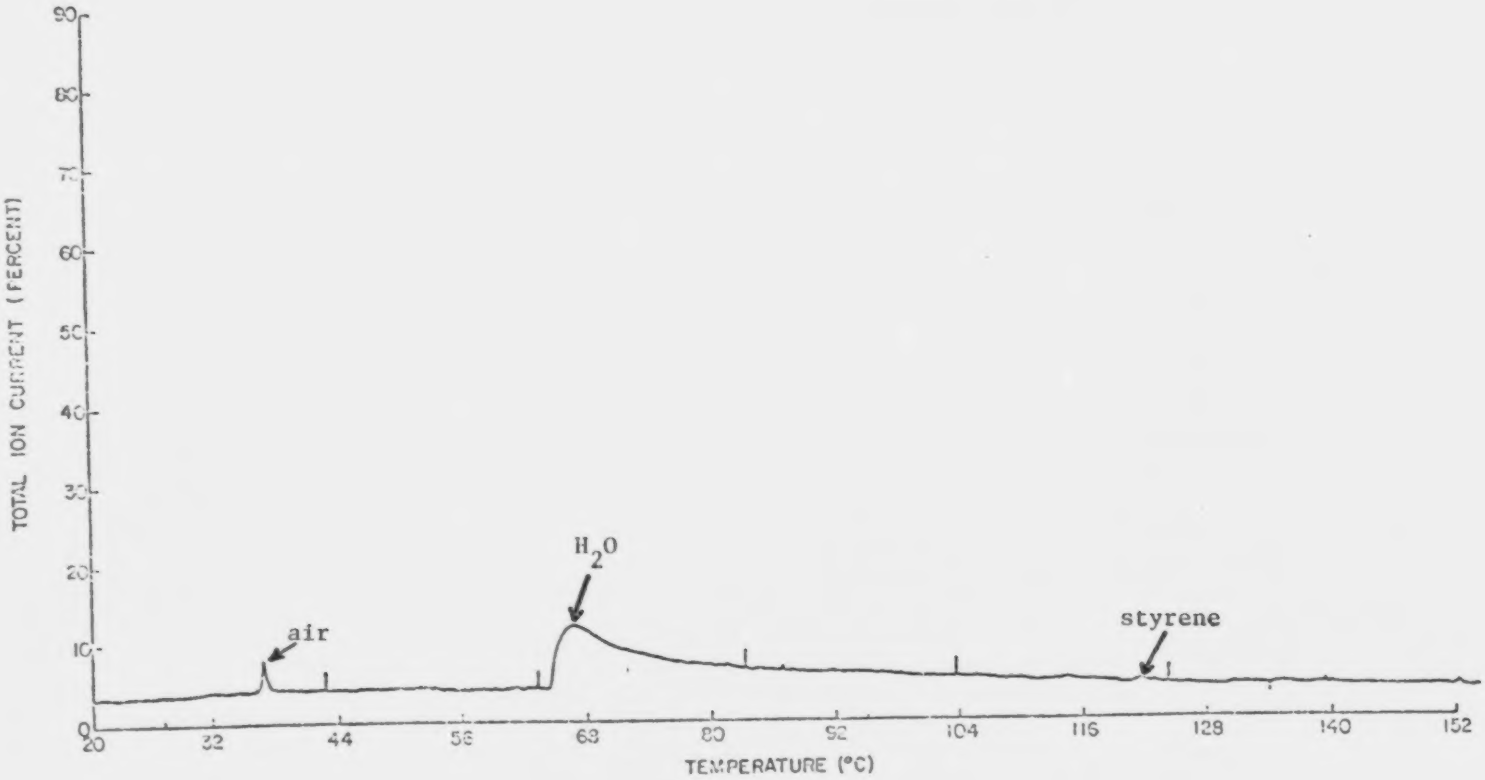

Figure F3. Background profile for Tenax GC cartridge blank.

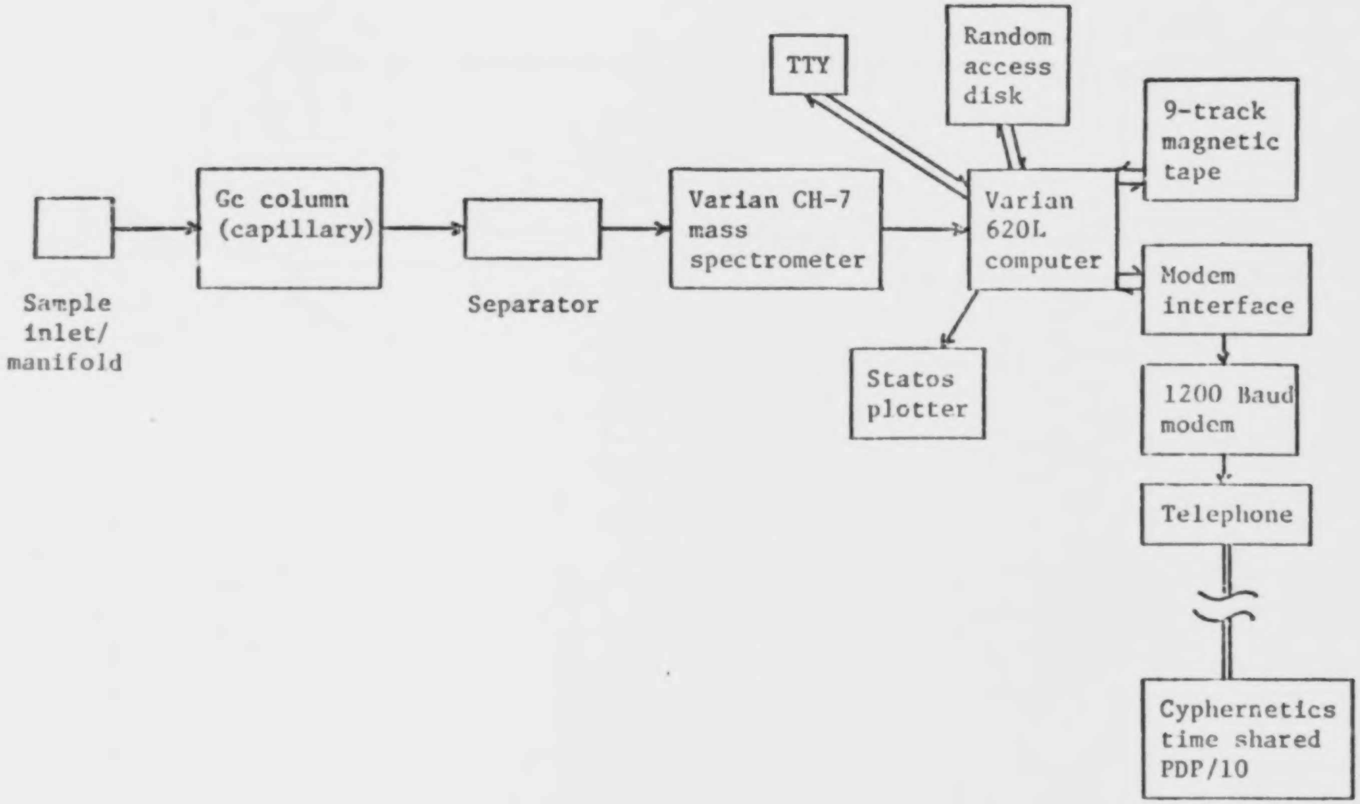
Sample inlet/ manifold
Gc column (capillary)
Separator
Varian CH-7 mass spectrometer
TTY
Random access disk
Varian 620L computer
Statos plotter
9-track magnetic tape
Modem interface
1200 Baud modem
Telephone
Cyphernetics time shared PDP/10

Figure F4. Schematic diagram of gc-ms computer system

generated will be stored in the 620/L computer memory. This calibration serves only to calibrate the mass ion over the mass scanning range.

While the magnetic is continuously scanning the sample is injected and automatic data acquisition is initiated. As each spectrum is acquired by the computer each peak which exceeds a preset threshold is recognized and reduced to centroid time and peak intensity. This information is stored in the computer core while the scan is in progress. In addition, approximately 30 total ion current values and an equal number of Hall probe signals are stored in the core of the computer as they are acquired. During the 3 second period between scans this spectral information, along with the spectrum number, is written sequentially on disks, and the computer is reset for the acquisition of the next spectrum.

This procedure continues until the entire gc run is completed. By this time there are from 300-1,000 spectra on the disk which are then subsequently processed. Depending on the information required, the data may then either be processed immediately or additional samples may be run, stored on magnetic tape and the results examined at a later time.

The mass spectral data are processed in the following manner. First, the original spectra are scanned and the total ion current (TIC) information is extracted. Then the TIC intensities are plotted against the spectrum number on the Statos 31 recorder. The information will generally indicate whether the run is suitable for further processing, since it will give some idea of the number of unknowns in the sample and the resolution obtained using the particular glc column conditions.

The next stage of the processing involves the mass conversion of the spectral peak times to peak masses which is done directly via the dual disk system. The mass conversion is accomplished by use of the calibration table obtained previously using perfluorokerosene. Normally one set of the calibration data is sufficient for an entire day's data processing since the characteristics of the Hall probe are such that the variation in calibration is less than 0.2 atomic mass units/day. A typical time required for this conversion process for 1,000 spectra is approximately 30 min.

After the spectra are obtained in mass converted form, processing proceeds either manually or by computer. In the manual mode the full spectra of scans from the gc run are recorded on the Statos 31 plotter. The TIC information available at this time is most useful for deciding which spectra are to be analyzed. At the beginning of the runs where peaks are very sharp nearly every spectrum must be inspected individually to determine the identity of the component. Later in the chromatographic run when the peaks are broader only selected scans need to be analyzed.

Identification of resolved components is achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra (9). Individual difficult unknowns are searched by the use of the Cornell University STIRS and PBM systems. Unknowns are also identification of unknowns are confirmed by comparing the cracking pattern and elution temperatures for two different chromatographic columns (OV-101 and OV-17 SCOT capillaries) for the unknown and authentic compounds. The relationship between the boiling point of the identified halogenated hydrocarbon and the elution temperature on a non-polar column (the order of elution of constituents is predictable in homologous series since the OV-101 SCOT capillary separates primarily on the basis of boiling point) is carefully considered in making structure assignments.

Mass spectra search programs are operational at the Triangle Universities Computation Center (TUCC). RTI maintains thrice daily service to TUCC, which is one-quarter mile distance from the RTI campus. Additional information about each magnetic tape containing the mass spectra of halogenated hydrocarbons is entered directly into the TUCC job stream using a remote job entry processing. This is normally done at TUCC using one of the five terminals located within the Analytical Sciences Laboratory. The control information contains selected spectrum numbers of instructions to process entire gc runs. The computer program systems compare simultaneously either the entire library of 25,000 compounds or some subset of this library. The complete reports showing the best fits for each of the unknowns is produced at TUCC and printed out at the high speed terminals located on the RTI campus of TUCC. Thus, the processing of the mass spectral data obtained for the halogenated hydrocarbons in the samples collected is processed by one of three routes. Each consists of a different level of effort. The first level is strictly a manual interpretation process which proves to be the most thorough approach. The second level is executed when the interpretation at the first level has not yielded conclusive results.

8.4.2 Quantitative Analysis

In many cases the estimation of the level of pollutants by capillary gas chromatography in combination with mass spectrometry is not feasible utilizing only the total ion current monitor (see Fig. F2 for example), since baseline resolution between peaks is not always achieved. We employ the techniques which have been previously developed under contract whereby full mass spectra are obtained during the chromatographic separation step and then selected ions are presented as mass fragmentograms using computer software programs which allow the possibility of deconvoluting constituents which were not resolved in the total ion current chromatogram (6). Examples are depicted in Figures F5 and F6 which represent an ambient air sample with an TIC profile as in Fig. F2.

In our gc/ms/comp system we request from the Varian 620L dedicated computer mass fragmentograms for any combination of m/e ions when full mass spectra are obtained during chromatography. Thus, selectivity is obtained by selecting the unique ion for that particular halogenated hydrocarbon, and this is represented versus time with subsequent use of that ion intensity for quantitation. Also, quantitation with external standards is easily achieved using the intensity of the total ion current monitor or the use of a unique mass cracking ion in the mass spectrum of that external standard. Thus, we use mass fragmentography for the quantitation of halogenated hydrocarbons in ambient air when the total ion current is inadequate because of a lack of complete resolution between components in the mixture.

As described previously, the quantitation of constituents in ambient air samples is accomplished either by utilizing the total ion current monitor or where necessary the use of mass fragmentograms. In order to eliminate the need to obtain complete calibration curves for each compound for which quantitative information is desired, we use the method of relative molar response (RMR) factors (10). Successful use of this method requires information on the exact amount of standard added and the relationship of

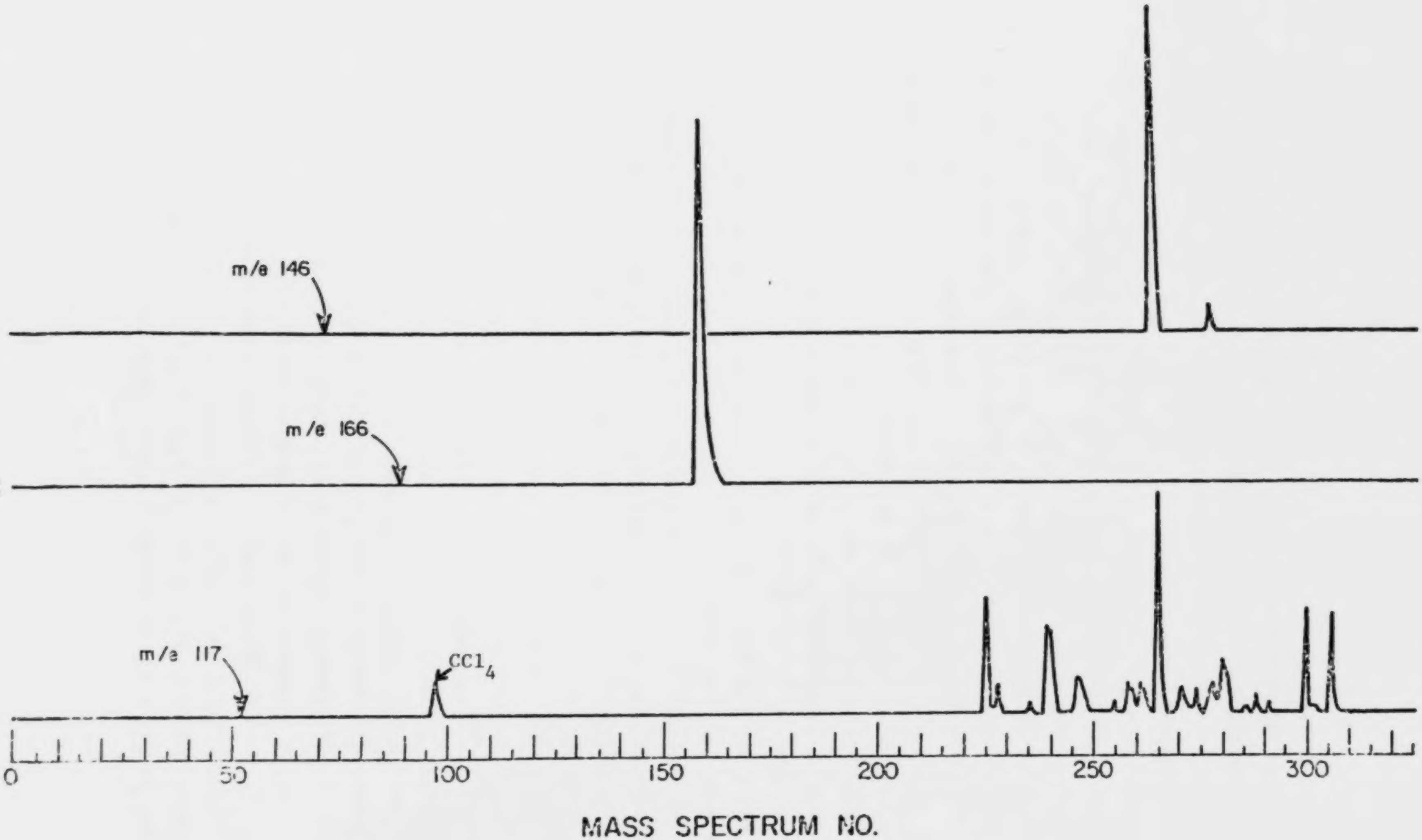

Figure F5. Mass fragmentograms of characteristic ions representing carbon tetrachloride (m/e 117), tetrachloroethylene (m/e 166) and m-dichlorobenzene (m/e 146) in ambient air.

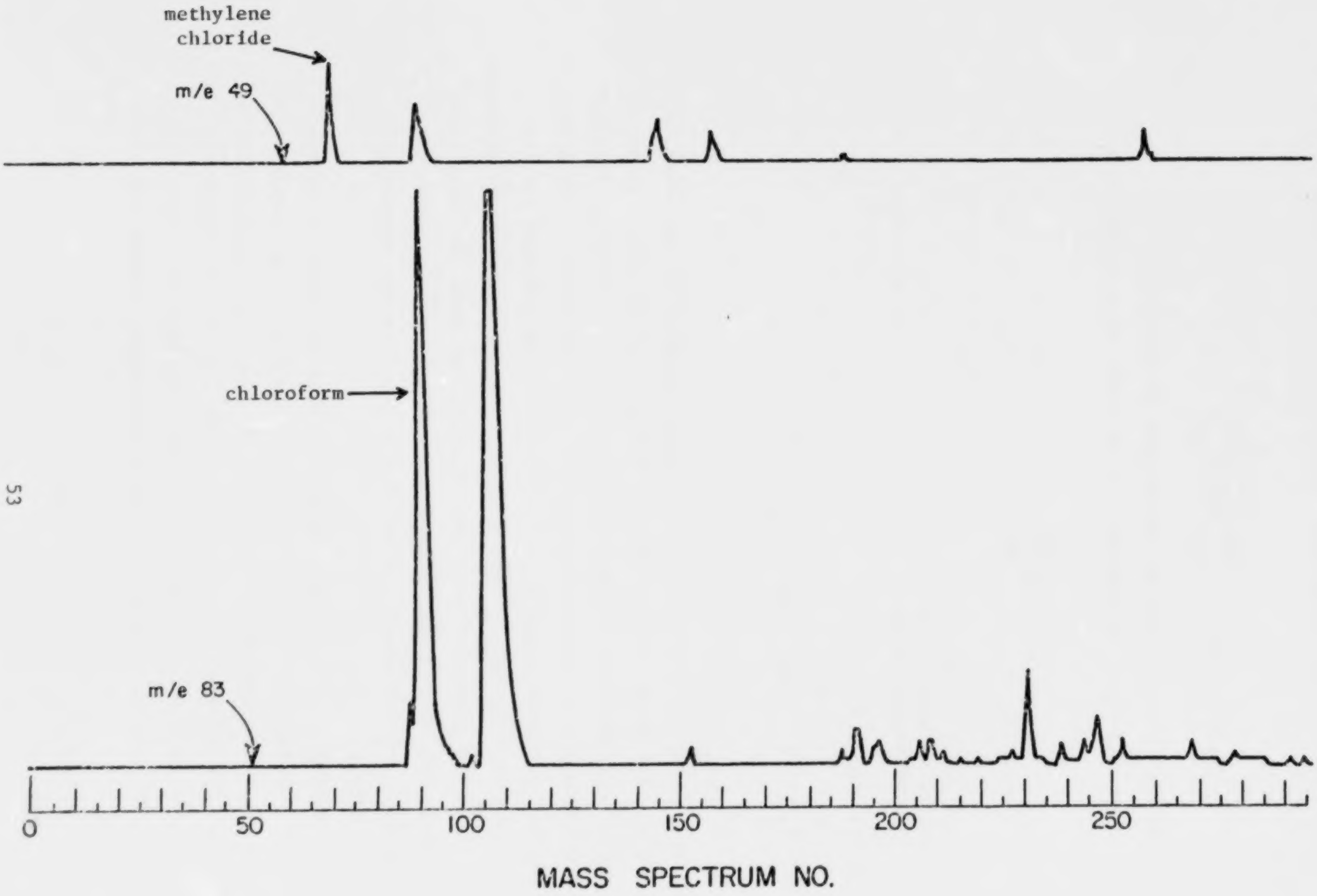

Figure F6. Mass fragmentograms of characteristic ions representing methylene chloride (m/e 49) and chloroform (m/e 83) in ambient air.

RMR (unknown) to the RMR (standards). The method of calculation is as follows:

$$(1)\quad RMR_{unknown/standard} = \frac{A_{unk}/Moles_{unk}}{A_{std}/Moles_{std}}$$

A = peak area, determined by integration or triangulation.

The value of RMR was determined from at least three independent analyses.

$$(2)\quad RMR_{unk/std} = \frac{A_{unk}/g_{unk}/GMW_{unk}}{A_{std}/g_{std}/GMW_{std}}$$

A = peak area, as above
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$(3)\quad g_{unk} = \frac{A_{unk} \cdot GMW_{unk} \cdot g_{std}}{A_{std} \cdot GMW_{std} \cdot RMR_{unk/std}}$$

The standard added can be added as an internal standard during sampling. However since the volume of air taken to produce a given sample is accurately known, it is also possible and more practical to use an external standard whereby the standard is introduced into the cartridge prior to its analysis. Two standards, hexafluorobenzene and perfluorotoluene are used for the purpose of calculating RMR's. From previous research it has been determined that the retention times for these two compounds are such that they elute from the glass capillary column (OV-101) at a temperature and retention time which does not interfere with the analysis of unknown compounds in ambient air samples.

Since the volume of air taken to produce a given sample is accurately known and an external (or internal) standard is added to the sample, then the weight can be determined per cartridge and hence the concentration of the unknown. The approach for quantitating ambient air pollutants requires that the RMR is determined for each constituent of interest. This means that when an ambient air sample is taken, the external standard is added during the analysis at a known concentration. It is not imperative at this point to know what the RMR of each of the constituents in the sample happens to be; however, after the unknowns are identified, then the RMR can be subsequently determined and the unknown concentration calculated in the original sample using the RMR. In this manner it is possible to obtain qualitative and quantitative information on the same sample with a minimum of effort.

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Analytical protocol revised 1/24/77.

G. CHLORINE/BROMINE SAMPLING AND ANALYSIS IN AMBIENT AIR

1.0 Principle of Method

Gaseous chloride and bromide (HCl and HBr) are collected in deionized water in an impinger. The impinger solution is assayed for total halide by precipitation of the silver halide and determining the precipitate by turbidity or nephelometry. Another aliquot is subjected to ion exchange chromatography to separate chloride and bromide ion. The two fractions are analyzed bv the turbidity of the silver halide precipitate. Confirmation is obtained for bromide by neutron activation analysis.

2.0 Range and Sensitivity

Samples of ambient air are taken at 2 ℓ/min for a period of 30 min for a total of 60 ℓ of air using 20 ml of absorber solution. This period may be increased to 150 min or a total of 300 ℓ in the absence of strong oxidants.

The range of the turbidimetric method for total halides is 0.2 μg/ml to above 40 μg/ml in the absorber solution. The ion exchange chromatography is limited by recoveries and background to 1 μg/ml on the lower limit and to 5 mg/ml by ion exchange capacity at the upper limit.

Method	Range
Total halides (turibidity)	0.2 - 40 μg/ml
Ion exchange and turbidity	
chloride	1 - 500 μg/ml
bromide	1 - 1000 μg/ml
Neutron Activation	0.015 μg - 1 g/g

3.0 Interferences

Sampling - High concentration of strong oxidants (*i.e.*, Cl_2, O_3 ...) will oxidize bromide to bromine which is purged from the absorber solution resulting in low values for bromide. If the oxidant is chlorine then elevated chloride values would be obtained.

Total Halides - Phosphate

Ion Exchange and Turbidity - None known

Neutron Activation Analysis - Large quantities of sodium or potassium interfer. Organic bromine is measured as well as inorganic.

4.0 Precision and Accuracy

Sampling - With the use of syringe needles as critical orifices for flow control sample volumes can be collected with an accuracy 5% and a precision of 2%.

Total Halide - The precision of the silver halide turbidity method ranges from 6 to 1% over the concentration range 1 to 20 μg/ml in the absorber solution. Accuracy of the method depends upon the sample composition since the response is slightly halide dependent. Bromine gives 80% of the chloride response for the same weight.

Ion Exchange Chromatography and Turbidity - The precision of the measurement of chloride and bromide is 5% over the range 1.0 to 100 μg/ml of chloride and 1.0 to 100 μg/ml bromide in the impinger solution. The accuracy depends upon the assessment of recoveries and may introduce errors of up to 10%.

5.0 Apparatus

5.1 Sample Collection

Midget Impingers

Critical Oriface - 1 in. 21 gauge Becton Dickinson syringe needle.

Critical Oriface Protector - 6 inch drying tube packed with ascarite (20-30 mesh) retained by glass wool plugs at either end.

Pump - Adequate to produce 15 in Hg at 2 ℓ/min fitted with a rubber tubing manifold.

One ounce polyethylene bottles sufficient to ship the collected impinger solutions.

5.2 Turbidimetric Analysis

Adequate and sufficient storage bottles

1 - 1000 ml volumetric flask

8 - 100 ml volumetric flasks

1 - 15 ml volumetric pipette

1 - 2 ml volumetric pipette

3 - 1 ml volumetric pipettes

1 - 0.5 ml volumetric pipette

Sufficient 1 inch test tubes and 10 mm cuvettes for the number of samples and standards.

Vortex-type test tube stirrer.

Spectrophotometer or nephelometer capable of operating at 360 nnm.

5.3 Chromatography Apparatus

Chromatography Columns - 4 mm x 100 mm with a glass wool plug (thistle tubes with drawn tips at 10 cm are available).

Pipets - Graduated 2 and 5 ml.

Sample Bottles - 1 oz. sufficient for the collection of fractions.

6.0 Reagents

6.1 Sampling

Impinger Solution - 20 ml deionized water for each sample taken.

6.2 Turbidimetric Analysis

Silver Nitrate Solution (0.5 N) - Place 8.5 g $AgNO_3$ in a 100 ml volumetric flask and dilute to the mark with distilled or deionized water. Store in a dark brown bottle.

Nitric Acid (2.5 N) - Dilute 16 ml of concentrated HNO_3 to the mark in a 100 ml volumetric flask with deionized water.

Isopropanol - Reagent Grade

Stock Standard Chloride Solution - Weigh out 0.1648 g NaCl and place in a 100 ml volumetric flask. Dilute to the mark with deionized water. This solution contains 1000 μg Cl^-/ml.

Diluted Chloride Standards - A working standard is prepared by pipeting 10 ml of the stock chloride solution into a 100 ml volumetric flask and dilute to mark with deionized water. Pipet 0.5, 1, 5, 10 and 20 ml of the stock chloride standard solution into 100 ml volumetric flasks and dilute each to the mark with deionized water. These solutions contain respectively, 0.5, 1.0, 5, 10, and 20 μg Cl^-/ml.

6.3 Chromatography

0.1M Sodium Nitrate - Place 8.5 g $NaNO_3$ in a 1000 ml volumetric flask and dilute to the mark with deionized water.

0.5M Sodium Nitrate Place 42.5 g $NaNO_3$ in a 1000 ml volumetric flask and dilute to the mark with deionized water.

Anion Exchange Resin - AG-1-X10 (BioRad) converted to NO_3^- form by flushing with 0.5M $NaNO_3$ until a negative chloride test is obtained.

Dilute Chloride Standards for Chromatography - A working standard is parepared by pipeting 10 ml of the stock chloride solution (see Section 6.2) into a 100 ml volumetric flask and dilute to mark with 0.1 $\underline{M}$ $NaNO_3$. Pipet 0.5, 1, 5, 10, and 20 ml of the stock chloride standard solution into 100 ml volumetric flasks and dilute each to the mark with 0.1 $\underline{M}$ $NaNO_3$. These solutions contain respectively, 0.5, 1.0, 5, 10, and 20 μg Cl^-/ml.

Stock Standard Bromide Solution - Weigh out 0.1268 g NaBr and place in 100 ml volumetric flask. Dilute to the mark with deionized water. This solution contains 1000 μg Br^-/ml.

Diluted Bromide Standards - Prepare as for chloride using the stock standard bromide solution and making all dilutions with 0.5 $\underline{M}$ $NaNO_3$.

Silver Nitrate Solution, Nitric Acid, and isotropanol is described in Section 6.2.

7.0 Procedure

7.1 Sample Collection

Collect samples at 1.5-2 ℓ/min for 30 min periods. Laboratory evaluations have indicated sampling periods are reliable up to 150 min periods (300°) except for the displacement of bromide by change oxidants.

7.2 Turbidimetric Method for Halides

Place an aliquot of 3.0 ml of isopropyl alcohol and 0.2 ml 2.5$\underline{N}$ nitric acid in each of six 1 inch test tubes. To the first test tube add 1.6 ml of deionized water (the chloride blank). To tubes 2 through 6 add 1.6 ml aliquots of chloride standard at 0.5, 1, 5, 10 and 20 μg/ml. Mix using a Vortex type stirrer. Add 0.2 ml aliquot of 0.5$\underline{N}$ $AgNO_3$ to each test tube and mix the contents on the Vortex mixer. Store the resulting solutions in the dark for one hour and make nephelometric measurements of the turbidity at 360 nm. Plot turbidance vs μg Cl^-/ml to give a standard curve.

Samples of the impinger solution are analyzed as described for the standards.

7.3 Ion Exchange Separation of Chloride and Bromide

Chromatographic columns (4 x 70 mm) will be filled to 70 mm with AG-1-X10 anion exchange resin (BioRad) washed with 20 ml 0.5$\underline{M}$ $NaNO_3$. Wash the column with 5 ml of deionized water and add the sample (4 ml) to the column. Wash with 0.5 ml aliquot of deionized water. Elute the column with 4 ml of

0.1M $NaNO_3$ and collect for chloride analysis. Elute the bromide with a 2 ml aliquot of 0.5M $NaNO_2$. This fraction is used for the bromide analysis.

Place an aliquot of 3.0 ml of isopropyl alcohol and 0.2 ml 2.5N nitric acid in each of 12 test tubes. To the first test tube add 1.6 ml of 0.1M $NaNO_3$ (the chloride blank) to the second 1.6 ml of 0.5M $NaNO_3$ (the bromide blank). To tubes 3 through 7 add 1.6 ml aliquots of chloride standards diluted in 0.1M $NaNO_3$ to 0.5, 1, 5, 10, and 20 µg/ml. To tubes 8 through 12 add 1.6 ml aliquots of bromide standards dilute in 0.5M $NaNO_3$ to 0.5, 1, 5, 10 and 20 µg/ml. Mix using a Vortex type stirrer. Add an aliquot of 0.5 ml of 0.5N $AgNO_3$ to each test tube and mix the contents on the Vortex mixer. Store the resulting solutions in the dark for one hr and make nephelometric measurements of the turbidity at 360 nm. Plot turbidance *vs* µg Cl^-/ml or µg Br^-/ml to give a standard curve.

Repeat the same procedure for 1.6 ml aliquots of the chloride and bromide fractions. Read concentrations from the appropriate standard curve.

8.0 Calibration Methods

Calibration of the analytical methods will be done using sodium chloride and sodium bromide as standards. Verification of collection efficiency and breakthrough will be obtained by volatilizing aliquots containing known amounts of HCl and HBr in the air stream entering the impinger.

9.0 Calculations

9.1 Total Halide (as HCl)

$$\mu g\ HCl/M^3 =$$

$$\frac{\mu g\ Cl^-/ml \times ml\ absorber}{M^3\ sampled} \times \frac{36.45}{35.45}$$

9.2 Ion Exchange Separation of Chloride and Bromide

Gaseous Chlorides

e.g., HCl

$$\mu g\ HBr/M^3 =$$

$$\frac{\mu g\ Cl^-/ml \times ml\ column\ fraction \times ml\ absorber}{M^3\ sampled \times ml\ aliquot\ placed\ on\ column} \times \frac{36.45}{35.45}$$

Gaseous Bromides

e.g., HBr

$$\mu g\ HBr/M^3 = \frac{\mu g\ Br^-/ml \times ml\ column\ fraction \times ml\ absorber}{M^3\ sampled \times ml\ aliquot\ not\ placed\ on\ column} \times \frac{80.91}{79.91}$$

10.0 Effects of Storage

Glass containers must be avoided for the storage of dilute solutions of halides as they are adsorbed to the walls. For this reason polyethylene will be used for storage containers. In any case prompt analysis is highly desirable to obtain the most accurate results.

11.0 References

1. "Determination of Chlorine and/or Chlorides - Turbidimetric Method", Adopted January 31, 1975, Texas Air Control Board.
2. R. C. DeGeiso, W. Rieman and S. Linderbaum, Anal. Chem., 26, 1840 (1954).
3. H. D. Axelrod, J. E. Bonelli and J. P. Lodge, Jr., Environ. Sci. Tech., 5, 420 (1971).

Analytical protocol revised 1/24/77.

H. CHLORINE/BROMINE SAMPLING AND ANALYSIS IN AMBIENT AIR

1.0 Principle of Method

Gaseous chlorine and bromine are collected in alkaline sodium arsenite in an impinger. The halogens are reduced to the corresponding halides and are not volatile in the alkaline solution. Hydrogen chloride and hydrogen bromide are removed by passing the air sample through an impinger containing deionized water prior to the alkaline sodium arsenite. The impinger solution is assayed for total halide by precipitation of the silver halide and determining the precipitate by turbidity or nephelometry. Another aliquot is subjected to ion exchange chromatography to separate chloride and bromide ion. The two fractions are analyzed by the turbidity of the silver halide precipitate. Confirmation is obtained from bromide by neutron activation analysis.

2.0 Range and Sensitivity

Samples of ambient air are taken at 2 ℓ/min for a period of 30 min for a total of 60 ℓ of air using 20 ml of absorber solution. This period may be increased to 150 min or a total of 300 ℓ.

The range of the turbidimetric method for total halides is 0.2 μg/ml to above 40 μg/ml in the absorber solution. The ion exchange chromatography is limited by recoveries and background to 1 μg/ml on the low level and to 5 mg/ml by ion exchange capacity at the upper limit.

Method	Range
Total halides (turbidity)	0.2 - 40 μg/ml
Ion exchange and turbidity	
chloride	1 - 500 μg/ml
bromide	1 - 500 μg/ml
Neutron Activation	0.015 μg - 1 g/g

3.0 Interferences and Problems Anticipated

Sampling - The disposition of chlorine in the impinger train in the absence of bromide is known. Bromine is purged through the impinger train unless a large volume (300 ℓ) is sampled. Even then 8 to 23% is found in the deionized water. High concentration of strong oxidants (i.e., Cl_2, O_3 ...) oxidize bromide collected in the first impinger to bromine leading to high bromine values. If the oxidant is chlorine then low chlorine values are obtained.

Total Halides - Phosphates

Ion Exchange and Turbidity - None known

Neutron Activation Analysis - Large quantities of sodium or potassium interfer. Organic bromine is measured as well as inorganic.

4.0 Precision and Accuracy

Sampling - With the use of syringe needles as critical orifices for flow control sample volumes can be collected with an accuracy 5% and a precision of 2%. Accuracy of sampling is subject to the limitations described in Section 3.0.

Total Halide - The precision of the silver halide turbidity method ranges from 6 to 1% over the concentration range 1 to 20 µg/ml in the absorber solution. Accuracy of the method depends upon the sample composition since the response is halide dependent.

Ion Exchange Chromatography and Turbidity - Concentration dependent recoveries result in standard deviations which are 10 and 5% relative at 355 µg/ml chloride (10^{-2}M) and 790 µg/ml (10^{-2}M) bromide, respectively, but 30% at 3.5 µg/ml chloride and 7.9 µg/ml bromide.

5.0 Apparatus

5.1 Sample Collection

Critical Oriface - 1 in. 21 gauge Becton Dickinson syringe needle.

Critical Oriface Protector - 6 inch drying tube packed with ascarite (20-30 mesh) retained by glass wool plugs at either end.

Pump - Adequate to produce 15 in Hg at 2 ℓ/min fitted with a rubber tubing manifold.

One ounce polyethylene bottles sufficient to ship the collected impinger solutions.

5.2 Turbidimetric Analysis

Adequate and sufficient storage bottles

1 - 1000 ml volumetric flask

8 - 100 ml volumetric flasks

1 - 15 ml volumetric pipette

1 - 2 ml volumetric pipette

3 - 1 ml volumetric pipettes

1 - 0.5 ml volumetric pipettes

Sufficient 1 inch test tubes and 10 mm cuvettes for the number of samples and standards.

Vortex-type test tube stirrer

Spectrophotometer or nephelometer capable of operating at 360 nm.

5. Chromatography Apparatus

Chromatography columns - 4 mm x 100 mm with glass wool plug (thistle tubes with drawn tips at 10 cm are suitable).

Pipets - Graduated 10 and/or 20 ml.

Sample Bottles - 1 oz sufficient for the collection of fractions.

6.0 Reagents

6.1 Sampling

Impinger Solution A - 20 ml deionized water for each sample taken and Impinger Solution B - 20 ml of solution which contains 4 grams NaOH and 0.65 gram $NaAsO_2$ in a 1000 ml volumetric flask and dilute to the mark with deionized water.

6.2 Turbidimetic Analysis

Silver Nitrate Solution (0.5 N) - Place 8.5 g $AgNO_3$ in a 100 ml volumetric flask and dilute to the mark with distilled or deionized water. Store in a dark brown bottle.

Nitric Acid (2.5 N) - Dilute 16 ml of concentrated HNO_3 to the mark in a 100 ml volumetric flask with deionized water.

Isopropanol - Reagent Grade

Stock Standard Chloride Solution - Weigh out 0.1648 g NaCl and place in a 100 ml volumetric flask. Dilute to the mark with deionized water. This solution contains 1000 µg Cl^-/ml.

Diluted Chloride Standards - A working standard is prepared by pipeting 10 ml of the stock chloride solution into a 100 ml volumetric flask and dilute to mark with deionized water. Pipet 0.5, 1, 5, 10 and 20 ml of the stock chloride standard solution into 100 ml volumetric flasks and dilute each to the mark with deionized water. These solutions contain respectively, 0.5, 1.0, 5, 10, and 20 µg Cl^-/ml.

6.3 Chromatography

Sodium Nitrate 0.1M - Place 8.5 g $NaNO_3$ in a 1000 ml volumetric flask and dilute to the mark with deionized water.

Sodium Nitrate 0.5M - Place 42.5 g $NaNO_3$ in a 1000 ml volumetric flask and dilute to the mark with deionized water.

Anion Exchange Resin - AG-1-X10 (BioRad) converted to NO_3^- form by flushing with 0.5M $NaNO_3$ until a negative chloride test is obtained.

Dilute Chloride Standards for Chromatography - A working standard is prepared by pipeting 10 ml of the stock chloride solution (see Section 6.2) into a 100 ml volumetric flask and dilute to mark with 0.1M $NaNO_3$. Pipet 0.5, 1, 5, 10, and 20 ml of the stock chloride standard solution into 100 ml volumetric flasks and dilute each to the mark with 0.1M $NaNO_3$. These solutions contain respectively, 0.5, 1.0, 5, 10, and 20 μg Cl^-/ml.

Stock Standard Bromide Solution - Weigh out 0.1288 g NaBr and place in 100 ml volumetric flask. Dilute to the mark with deionized water. This solution contains 1000 μg Br^-/ml.

Dilute Bromide Standards - Prepare as for chloride using the stock standard bromide soluion and making all dilutions with 0.5M $NaNO_3$.

Silver Nitrate Solution, Nitric Acid, and isopropanol as described in Section 6.2.

7.0 Procedure

7.1 Sample Collection

Collect samples at 1.5-2 ℓ/min for 30 min period. Laboratory evaluation indicated longer sampling periods are reliable and this time period may be increased to 150 min.

7.2 Turbidimetric Method for Halides

Place an aliquot of 3.0 ml of isopropyl alcohol and 0.2 ml of 2.5N nitric acid in each of six 1 inch test tubes. To the first test tube add 1.6 ml of deionized water (the chloride blank). To tubes 2 through 6 add 1.6 ml aliquots of chloride standard at 0.5, 1, 5, 10 and 20 μg/ml. Mix using a Vortex type stirrer. Add an aliquot of 0.2 ml of 0.5N $AgNO_3$ to each test tube and mix the contents on the Vortex mixer. Store the resulting solutions in the dark for one hour and make nephelometric measurements of the turbidity at 360 nm. Plot turbidance *vs* /g Cl^-/ml to give a standard curve.

Samples of the impinger solution will be treated as described for the standards.

7.3 Ion Exchange Separation of Chloride and Bromide

Chromatographic columns (4 x 100 mm) will be filled to 70 mm with AG-1-X10 anion exchange resin (BioRad) equilibrated with 0.5$\underline{M}$ $NaNO_3$. Wash the column with 5 ml of deionized water and add the sample (3 ml) to the column. Wash with 0.5 ml aliquot of deionized water. Wash the column with 4 ml aliquot of 0.1 $NaNO_3$ and collect the fraction for the chloride determination. Elute the bromide with a 2 ml aliquot of 0.5$\underline{M}$ $NaNO_3$. This fraction will be used for the bromide analysis.

Place an aliquot of 3.0 ml of isorporpyl alcohol and 0.2 ml 2.5$\underline{N}$ nitric acid in each of twelve test tubes. To the first test tube add 1.6 ml of 0.1$\underline{M}$ $NaNO_3$ (the chloride blank), to the second 1.6 ml of 0.5$\underline{M}$ $NaNO_3$ (the bromide blank). To tubes 3 through 7 add 1.6 ml aliquots of chloride standards diluted in 0.1$\underline{M}$ $NaNO_3$ to 0.5, 1, 5, 10, and 20 μg/ml. To tubes 8 through 12 add 1.6 ml aliquots of bromide standards diluted in 0.5$\underline{M}$ $NaNO_3$ to 0.5, 1, 5, 10 and 20 μg/ml. Mix using a Vortex type stirrer. Add an aliquot of 0.2 ml of 0.5$\underline{N}$ $AgNO_3$ to each test tube and mix the contents on the Vortex mixer. Store the resulting solutions in the dark for one hour and make nephelometric measurements of the turbidity at 360 nm. Plot turbidance *vs* μg Cl^-/ml or μg Br^-/ml to give a standard curve.

8.0 Calibration Methods

Calibration of the analytical methods will be done using sodium chloride and sodium bromide as stndards. Verification of collection efficiency and breakthrough will be obtained using Cl_2 and Br_2 permeation tubes.

9.1 Total Halogen (as Cl_2)

$$\mu g\ Cl_2/M^3 = \frac{\mu g\ Cl^-/ml \times ml\ absorber}{M^3\ sampled\ x}$$

9.2 Ion Exchange Separation of Chloride and Bromide

Chlorine

$$\mu g\ Cl_2/M^3 = \frac{\mu g\ Cl^-/ml \times ml\ column\ fraction \times ml\ absorber}{M^3\ sampled \times ml\ aliquot\ placed\ on\ column}$$

Bromine

$$\mu g\ Br_2/M^3 = \frac{\mu g\ Br^-/ml \times ml\ column\ fraction \times ml\ absorber}{M^3\ sampled \times ml\ aliquot\ placed\ on\ column}$$

10.0 Effects of Storage

Glass containers must be avoided for the storage of dilute solutions of halides as they are adsorbed to the walls. For this reason polyethylene will be used for storage containers. In any case prompt analysis is highly desirable to obtain the most accurate results.

11.0 References

1. "Determination of Chlorine and/or Chlorides - Turbidimetric Method", Adopted January 31, 1975, Texas Air Control Board.
2. R. C. Degeiso, W. Rieman and S. Linderbaum, Anal. Chem., 26, 1840 (1954).
3. H. D. Axelrod, J. E. Bonelli and J. P. Lodge, Jr., Environ. Sic. Tech., 5, 420 (1971).

Analytical protocol revised 1/24/77.

I. DETERMINATION OF INORGANIC FLUORIDE IN AMBIENT AIR

Adaptation of the Specific Ion Electrode Method for Measurement of Fluorede Ion in Gaseous Samples

1.0 Principle of Method

Gaseous fluoride and fluorine gas are absorbed in a caustic solution. A midget impinger is used and the exposed solution returned to the laboratory for processing.

After proper processing, the sample is treated with a buffer. The concentration of fluoride in the sample is determined using a fluoride specific ion electrode.

2.0 Range and Sensitivity

The concentration range for the actual analysis of the sample should be from 0.1 to 10.0 µg of fluoride total in the aliquot taken for the analyis. Hence, the lower limit of detection in the ambient air will depend upon the volume of air passed through the absorbing solution.

In general, levels in the low part per billion range of fluoride can be measured for gaseous samples.

3.0 Interferences

Substances which form stable fluoride complexes such as aluminum silicon and/or iron (III) interfer. Using TISAB® buffer up to 5 ppm of aluminum or ion does not interfer with the determination of 1 ppm F^-. If higher levels are encountered a tartarate-TRIS buffer TISAB® can be used to eliminate interference.

Cations and most anions do not interfere with the response of the fluoride elctrode to fluoride. Anions commonly associated with fluoride such as Cl^-, Br^-, I^-, $SO_4^=$, HCO_3^-, NO_3^-, PO_4^{-3} and acetate do not interfere with electrode operation. The OH^- ion is an electrode interference.* Some anions, such as $CO_3^=$ or PO_4^{-3}, make the sample more basic, increasing the OH^- interference, but are not direct electrode interferences.

4.0 Precision and Accuracy

The Orion Model 801 digital pH/mv meter used for the measurements is accurate to ±0.1 mV which over the nerstian region, 1 to 190 ppm, corresponds to 0.2%. Preparation of standards, temperature fluctuations represent the largest sources of error, but should not exceed 2%.

5.0 Apparatus

Midget impinger sampling train

1 - Steam distillation apparatus

1 - Evaporation oven

Sufficient and adequate sample storage bottles

1 - Specific fluoride ion electrode with accompanying meter[**]

1 - Saturated calomel reference electrode[**]

Sufficient number of 50 ml polyethylene beakers for the number of samples and standards being analyzed.

3 - 1000 ml volumetric flasks

1 - 500 ml volumetric flask

3 - 100 ml volumetric flasks

1 - 15 ml volumetric pipet

Sufficient 10 ml volumetric pipettes for the number of standards and samples being analyzed.

1 - 1 ml volumetric pipet

1 - 1 ml graduated pipet

6.0 Reagents

All reagents should be ACS reagent grade.

(1) Sodium Citrate Buffer (0.1 M) - Dissolve 35.72 g of sodium citrate ($2Na_3C_6H_5O_7 \cdot 11\ H_2O$) in approximately 750 ml of distilled water contained in a 1000 ml volumetric flask. After the salt is completely dissolved, dilute to the mark with distilled water and mix thoroughly.

NOTE---Buffers for this purpose are available commercially TISAB®, a product of Orion Research, is one which has been used in this laboratory.

(2) Sulfuric Acid - 96.0%.

(3) Sodium Hydroxide.

(a) 1.0 N Sodium Hydroxide - Carefully weigh out 20.0 grams of sodium hydroxide and place in a 500 ml volumetric flask. Add approximately 475 ml of distilled water and stir until the NaOH is completely dissolved. Allow the solution to cool and dilute to the mark with distilled water.

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[*] However proper use of buffers avoids this interference

[**] Combination specific fluoride ion electrode with accompanying meter may be substituted.

(b) 0.01 N Sodium Hydroxide - Place 10 ml of the 1.0 N NaOH in a 1000 ml volumetric flask. Dilute to the mark with distilled water. This solution serves as the absorbing reagent for the gaseous fluorides.

(4) Standard Fluoride Solution - Dissolve 0.2210 g of sodium fluoride in distilled water contained in a 1000 ml volumetric flask. Stir until the NaF is completely dissolved. The resulting solution is 1×10^{-2} M in F^- or 190 ppm.

7.0 Procedure

7.1 Pre-distillation, Preparation of the Sample

The sample from absorption of gaseous fluorides is generally evaporated down to a convenient volume of 15-20 ml. This evaporation also serves to concentrate the fluoride. No other preparation of this sample is needed prior to the steam distillation procedure. A blank should be run in parallel with the sample. If the occurance of interferences has been demonstrated to be low and fluoride is present in significant concentration, then an aliquot of the sample as received may be taken and the distillation step omitted.

7.2 Steam Distillation Procedure

Quantitiavely transfer the sample into the distilling flask from its container using several small quantities of water until the volume is approximately 30 ml. Using a volumetric pipet, add 15 ml of concentrated sulfuric acid. Next, add several crystals of silver nitrate. (Pherchloric acid may be used. However, due to the possible presence of organic carbonaceous material, perchloric acid can be extremely hazardous. Satisfactory results have been obtained using only sulfuric acid).

Place an aliquot of 1.0 ml of 0.1N sodium hydroxide in the distillate collector to fix the fluoride. Heat the steam generator and the distilling flask simultaneously with the line between the distilling flask and the steam generator closed and the steam generator vented to the atmosphere. Heat the steam generator until steam is emitted into the atmosphere. Heat the distilling flask to 145°C-140°C and close the atmospheric vent of the steam generator and open the line to the distilling flask.

As the steam passed through the distilling flask, it will enter the condenser tube, sweeping with it the fluoride compounds, HF and SiF_4. Both are condensed and collected in a receiving flask. Continue distillation until about 125 ml of condensate has been collected. It is necessary that the distillation period be of a duration so as to transfer the fluorides from the distillation flask to the collection flask, but not for such a long duration that the quantity of fluoride in the collection flask becomes so dilute that it is below the detection limits of the technique in use. (If this happens, the fluoride concentration can be increased by slow evaporation of the excess liquid volume). At this point, the sample is ready for analysis. The apparatus and glassware are easily contaminated with fluoride. If there is any possibility that such may have occurred, distill several 25 ml portions of distilled water checking the condensate from each run for its fluoride content before distilling any actual samples. If the samples analyzed have a wide range of concentrations, maintain two complete sets of glassware, one set for the "low" concentrations of fluoride and the other for the "high" concentrations of fluoride.

7.3 Detection by Fluoride Ion Selective Electrode

Standard Curve Preparation - Using volumetric pipettes place 0.1, 1.0 and 10.0 ml of the standard fluoride solution in 100 ml volumetric flasks. These standards contain 0.1, 1.0, and 10.0 μg fluoride per ml respectively.

Using 10 ml volumetric pipettes, transfer 10.0 ml of each of the standards to 50 ml polyethylene beakers (TISAB®) and mix thoroughly. Using the standards according to the manufacturer's instructions span and adjust the specific ion meter. Sample Analysis - To a 10 ml aliquot of the prepared sample, add 10 ml of the citrate buffer and measure the millivolts produced on the meter and compare with the prepared curve.

8.0 Calibration Method

Sodium fluoride will be used to prepare standards for the calibration of the pH/mv meter as described in Section 7.0. If steam distillation is used several samples must be distilled to evaluate recovery of fluoride. An HF permeation tube is available to evaluate the collection efficiency of the impinger.

9.0 Calculations

Gaseous

$$\mu g\ F^{-}/M^{3} = \frac{(\text{Conc. of aliquot analyzed})\ (\text{Total ml in condensate})\ (\text{Total ml in sample})}{(M^{3}\text{ of air})\ (\text{Aliquot analyzed})\ (\text{Total ml taken for distillation})}$$

10.0 Effects of Storage

Fluoride reacts with glass, therefore all storage containers must be plastic. No other special precautions are required.

11.0 References

1. "Determination of Inorganic Fluoride: Adaptation of the Specific Ion Electrode Method for Measurement of Fluoride Ion in Gaseous and Vegetative Samples", Adopted November 23, 1971, Texas State Department of Health, Air Pollution Control Services.
2. Operation Manual for Orion Fluoride Ion Selective Electrode.

Analytical protocol revised 1/24/77.

J. ACID MIST SAMPLING AND ANALYSIS IN AMBIENT AIR

1.0 Principle of Method

The acid aerosol is collected by filtration through filter papge. The collected acids are titrated directly and indirectly to compensate for neutralization by insolbule bases in the sample.

2.0 Range and Sensitivity

The upper limit is determined by the volume of the buret and titer of the base used. The lower limit is determined by the sensitivity of the indicator. For practical purposes this limit is 5 to 10 μg H_2SO_4 per sample.

3.0 Interferences

Acid gases such as sulfur dioxide, nitrogen dioxide, and carbon dioxide do not interfere in this method of filtration of acid aerosol. Basic gases, such as ammonia, may interfere and should be removed prior to filtration of the sample, if present in appreciable concentration. Particulate acids such as hydrochloric, phosphoric and nitric acid may be present in urban air and collected on filter paper. Interference by insoluble bases is overcome by use of the back titration procedure.

4.0 Precision and Accuracy

Precision and accuracy are dependent upon the precision and accuracy of the volume measurement of the titrant and the recognition of the end point. In the low μg range reproducibility should be 5 to 10% with visual and point detection. Photometric detection should improve that to 1 to 2%.

5.0 Apparatus

Micro buret

filter paper holder

Pump (Ex. Nutchel Model 221-A, Nutech Corp., Durham, N. C.).

Whatmann No. 1 Filter paper

6.0 Procedure

The acid aerosol is collected by filtration through 1-inch circles of Whatmann No. 1 filter paper at flow rates up to 30 ℓ/min over periods of 1-6 hours, depending upon the severity of the existing air pollution.

The filter paper is returned to the laboratory for analysis. The method of analysis involves titration of the filter papers to pH 7.

Prepare a solution of bromothymol blue in deionized water by adding 4 ml of a 0.1% solution of the indicator in alcohol to 100 ml of deionized water. To this solution add sufficient 0.01 N sodium tetraborate to produce a stable apple-green color (approx. pH 7). Cut the sample filter into two exactly equal portions, one portion being added to 1-2 ml of this solution and titrated with the standard tetraborate to the original green color. Keep a similar beaker containing the same volume of the solution as a control. Agitate during titration by vigorous swirling. The end point is reached after about 5 minutes. This end point is shown by a stable green color identical to that of the control solution.

The amount of acid indicated by this procedure has to be corrected for water-insoluble bases present in the sample, since some of the acid will react with these bases. The true amount of acid is found by adding a known excess of 0.01 N sodium tetraborate (at least 0.1 ml more than the amount indicated above) to the 1-2 ml of pH 7 solution and then immersing the second portion of the filter paper in it and titrate the excess with 0.01 N sulfuric acid.

7.0 Calibration Methods

The titer of the sodium tetraborate is determined against potassium acid phthalate, a primary standard.

8.0 Calculations

The concentration of acid, calculated as sulfuric acid in micrograms per cubic meter of air, is as follows:

$$\mu g\ H_2O_4 \qquad M^3 = \frac{98{,}000 \text{ X N X ml}}{V}$$

N = normality of sodium tetraborate (0.01 N)

ml = equivalent volume in milliliters of tetraborate solution to neutralize acid during back titration of half the filter paper sample

V = volume of air sampled (M^3)

9.0 Effects of Storage

The samples will need to be sealed against acid or basic atmosphere. Humidity may result in neutralization of sulfuric acid by insoluble bases in the sample.

10. References

1. Arthur C. Stern, Air Pollution, Vol. II, 2nd Edition, 1968, p. 77.

Analytical protocol revised 1/24/77.

K. SAMPLING AND ANALYSIS OF VOLATILE HALOGENATED HYDROCARBONS IN SOIL, SEDIMENT, WATER, VEGETATION AND MILK

1.0 Principle of the Method

Volatile compounds are recovered from an aqueous or solid sample by warming the sample and purging an inert gas through the warm sample. The vapors are then trapped on a Tenax cartridge which can be analyzed by thermal desorption interfaced to GC/MS for the ultimate analysis. The details of the purge procedure are dictated by the medium being analyzed as described below.

2.0 Range and Sensitivity

For a typical organic compound approximately 30 ng is required to obtain mass spectral identification using high resolution glass capillary GC/MS analysis. Based on a 50 g soil or sediment sample, a limit of detection of about 0.6 μg/kg would be typical. For water and milk, a 100 ml aliquot is used and the limit is then ~0.3 μg/ℓ. The vegetation sample size at 5 g permits the detection of compounds at ~6 μg/kg. The dynamic range for a purged sample is ~10^4, however, smaller samples may be purged and the ranged increased commensurately.

3.0 Interferences

Two possible types of interference must be considered: (1) material present in the sample which physically prevents the effective purge of the sample, and (2) a material which interferes with the analysis of the purged sample. In the former case, several techniques have been developed to handle such problems (e.g., foaming) by diluting and stirring the sample. The second case is minimized by the use of GC/MS for the analysis since unique combinations of m/e and retention time can be selected for most compounds. This permits the evaluation of compounds even though chromatographic resolution is not obtained.

4.0 Precision and Accuracy

The purge and trap technique has been evaluated using six model compounds which are expected to be typical of volatile halogenated compounds. These six (1-chloro-1-butene, 1,2-dichloroethane, 1-bromo-2-chloroethane, 1,2-dibromoethane, bromobenzene and m-chlorotoluene) were purged from distilled water, stream water and soil with recoveries of 60 to 102% for the water samples and 34 to 78% for the soil. Standard deviations for duplicate or triplicate analyses average 15%.

The precision of the purge step was not separated from the thermal desorption and apparatus to the GC.

5.0 Apparatus

5.1 Purge Apparatus

Two types of purge apparatus are required such as those shown in Figure K1.

5.2 Sampling Cartridges

The sampling tubes are prepared by packing a 10 cm long x 1.5 cm i.d. glass tube containing 6.0 cm of 35/60 mesh Tenax GC with glass wool in the ends to provide support (2,5). Virgin Tenax is extracted in a Soxhlet extractor for a minimum of 18 hours with acetone prior to preparation of cartridges samplers (2,5). After purification of the Tenax GC sorbent and drying in a vacuum oven at 100°C for 2-3 hr all of the sorbent material is meshed to provide a 35/60 mesh size range. Cartridge samplers are then prepared and conditioned at 270°C with helium flow at 30 ml/min for 30 minutes. The conditioned cartridges are transferred to Kimax® (2.5 cm x 150 cm) culture tubes, immediately sealed using Teflon lined caps and cooled. This procedure is performed in order to avoid recontamination of the sorbent bed (2,5).

5.3 Gas Chromatographic Column

A 0.35 mm i.d. x 100 m glass SCOT capillary column coated with OV-101 stationary phase and 0.1% benzyl triphenylphosphonium chloride is used for effecting the resolution of the halogenated hydrocarbons and other chemicals (5). The capillary column is conditioned for 48 hours at 230°C and 1.5-2.0 ml/min of helium flow. For highly polar pollutants of interest an 80 m Carbowax 20M glass SCOT capillary is used.

A Finnigan type glass jet separator on a Varian-MAT CH-7 GC/MS/COMP system is employed to interface the glass capillary column to the mass spectrometer. The glass jet separator is maintained at 240°C (2,5).

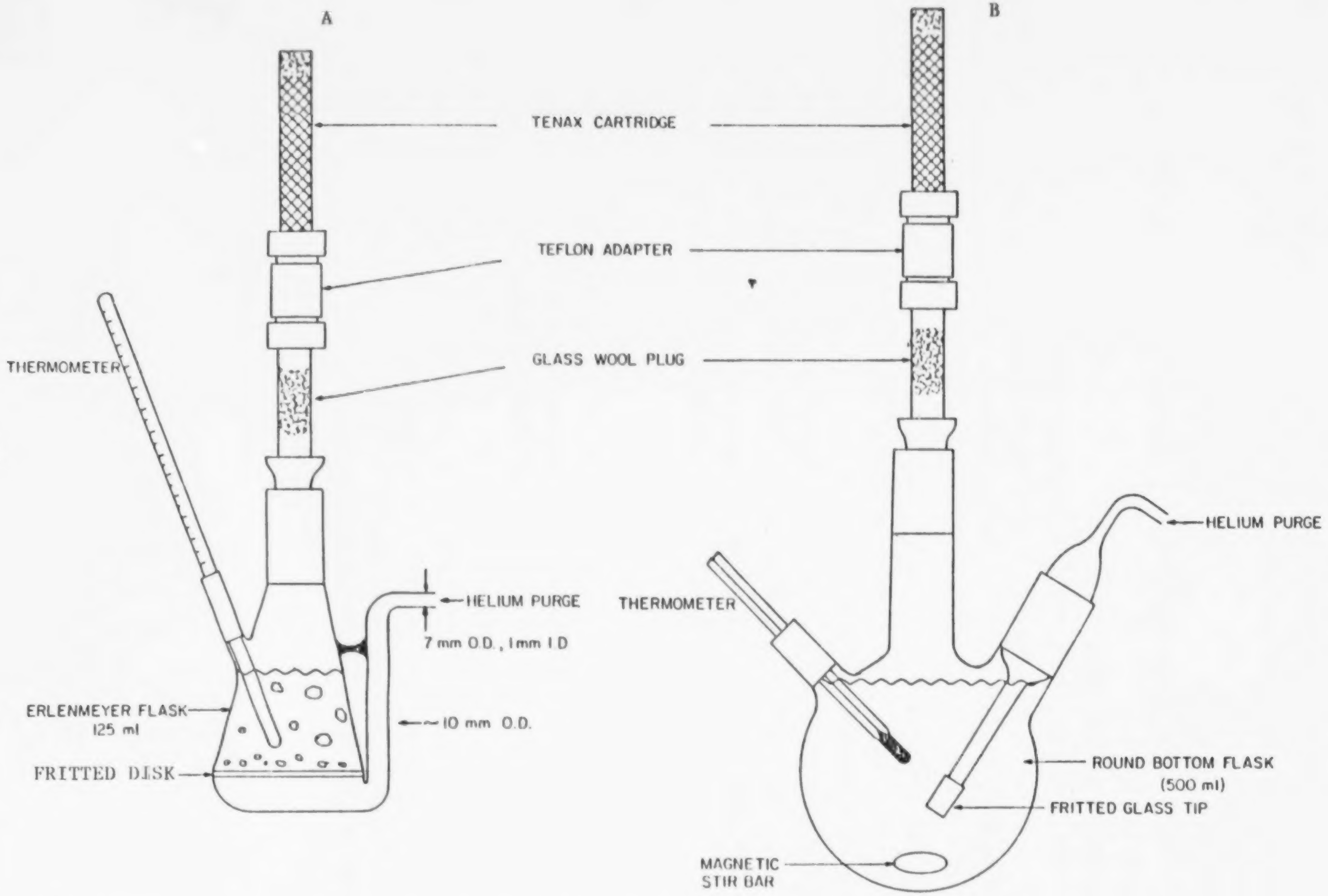
A
B
TENAX CARTRIDGE
TEFLON ADAPTER
GLASS WOOL PLUG
THERMOMETER
HELIUM PURGE
7 mm O.D., 1mm I.D
~10 mm O.D.
ERLENMEYER FLASK
125 ml
FRITTED DISK
THERMOMETER
HELIUM PURGE
ROUND BOTTOM FLASK
(500 ml)
FRITTED GLASS TIP
MAGNETIC
STIR BAR

Figure K1. Purge apparatus - A. Water samples; B. Soil, sediment, milk and vegetation.

5.4 Inlet Manifold

An inlet manifold for thermally recovering vapors trapped on Tenax sampling cartridges is employed and is shown in Figure K2 (1,2,4,5).

5.5 Gas Chromatograph

A Varian 1700 gas chromatograph is used to house the glass capillary column and is interfaced to the inlet manifold (Figure K2).

5.6 Mass Spectrometry/Computer

A Varian-MAT CH-7 mass spectrometer with a resolution of 2,000 equipped with a single ion monitoring capabilities is used in tandem with the gas chromatograph (Figure K2). The mass spectrometer is interfaced to a Varian 620/L computer (Figure K2).

6.0 Materials

6.1 Sampling

Adequate numbers of clean sample containers for the various media to be sampled. The media and the appropriate containers are listed below:

Soil and sediment - wide mouth, one liter glass bottles with foil lined caps.

Water - narrow mouth, one liter amber glass bottles with foil lined caps.

Vegetation - Wide mouth, one liter glass bottles with foil lined caps.

Milk - Tedlar® bags 36 x 36 cm.

6.2 Purge

Tenax cartridges - 16 mm o.d. x 10.5 cm glass tubes filled with six cm of Tenax with glass wool plugs in each end.

Charcoal cartridges - 16 mm o.d. x 6 cm filled with four cm of charcoal and glass wool plugs in each end.

Screw cap glass culture tubes.

7.0 Procedure

7.1 Collection of Field Samples

Soil samples are collected by taking cores with a garden bulb planter. The cores are placed in one liter wide mouth jars and sealed with foil lined caps. Water samples are collected in one liter narrow mouth amber jars. Vegetation is collected and stored in one liter, wide mouth jars. Milk is collected in glass and transferred to Tedlar® bags and frozen before shipping.

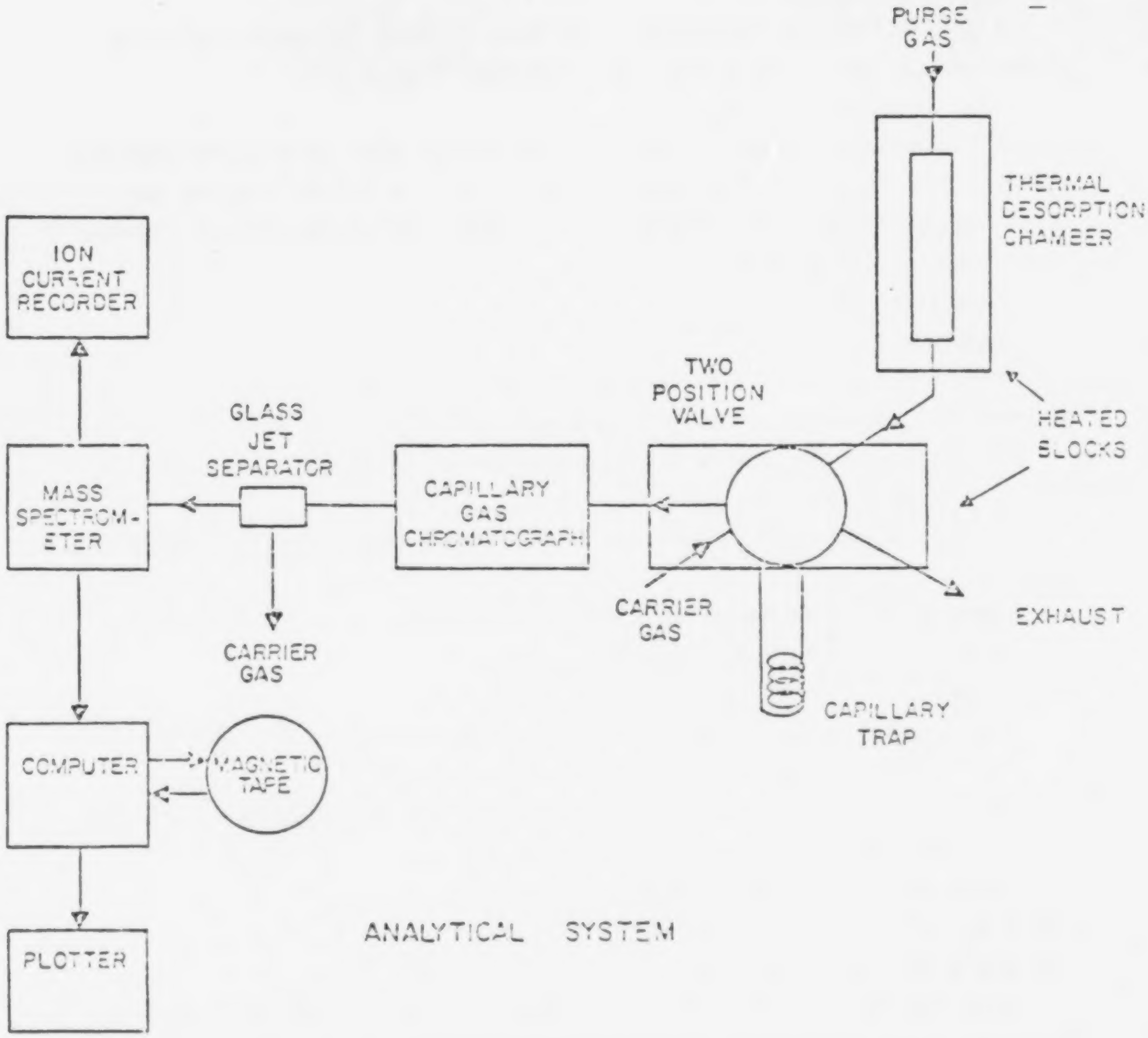
PURGE GAS
THERMAL DESORPTION CHAMBER
ION CURRENT RECORDER
TWO POSITION VALVE
HEATED BLOCKS
GLASS JET SEPARATOR
MASS SPECTROM-ETER
CAPILLARY GAS CHROMATOGRAPH
CARRIER GAS
EXHAUST
CARRIER GAS
CAPILLARY TRAP
COMPUTER
MAGNETIC TAPE
PLOTTER
ANALYTICAL SYSTEM

Figure K2. Vapor analytical systems for analysis of organic vapors in ambient air.

7.2 Purge of Volatile Organics

7.2.1 Water Samples

The water sample is cooled to ∿4°C and a 100 ml aliquot transferred to the purge apparatus. The apparatus is assembled as depicted in Figure K1a including the Tenax GC cartridge (1.5 cm diameter x 6.0 cm length). A carbon cartridge, 1.5 cm diameter x 4.0 cm length is encountered to the effluent end of the Tenax cartridge to prevent contamination of the cartridge by laboratory vapors. The flask is wrapped with heating tape and the sample heated to 90°C. The sample is purged at 25 ml helium/min and 90°C for 90 minutes. The loaded cartridge is removed and stored in a culture tube containing 1-2 g of $CaSO_4$ dessicant for at least two hrs. The dessicant is removed from the culture tube and the dry, loaded cartridge sotred at -20°C.

7.2.2 Soil and Sediment Samples

The apparatus assembled as depicted in Figure K1b including the Tenax GC cartridge (1.5 cm diameter x 6.0 cm length). A carbon cartridge, 1.5 cm diameter x 4.0 cm length is connected to the effluent end of the Tenax cartridge to prevent contamination of the cartridge by laboratory vapors. The soil or sediment sample is cooled to ∿4°C, 20 g transferred to the 500 ml flask and 450 ml of distilled water added. The mixture is stirred with a magnetic stirrer, heated to 90° with a heating mantle and purged at 25 ml helium/min and 90°C for 90 minutes. The loaded cartridge is removed and stored in a culture tube containing 1-2 g of $CaSO_4$ dessicant for at least two hrs. The dessicant is removed from the culture tube and the dry, loaded cartridge stored at -20°C.

7.2.3 Raw Milk Samples

The apparatus is assembled as depicted in Figure K1b including the Tenax GC cartridges (1.5 cm diameter x 6.0 cm length). A carbon cartridge 1.5 cm diameter x 4.0 cm length is connected to the effluent end of the Tenax cartridge to prevent contamination of the cartridge by laboratory vapors. The milk sample is cooled to ∿4°C, shaken vigorously and 100 ml diluted with 350 ml distilled water. The pH of the solution is adjusted to 4.0 with sulfuric acid. A glass wool plug is inserted into the center neck of the flask just above the level of the solution and with the flask in a heating mantle, the solution is heated to 70°C while stirring with a magnetic stirrer. The sample is purged at 15 ml helium/min and 70°C for 90 minutes. The loaded cartridge is removed and stored in a culture tube containing 1-2 g $CaSO_4$ dessicant for at least two hrs. The dessicant is removed from the culture tube and the dry, loaded cartridge stored at -20°C.

7.2.4 Vegetation Samples (Tentative)

The apparatus is assmbled as depicted in Figure K1b including the Tenax GC cartridge (1.5 cm diameter x 6.0 cm length). A carbon cartridge, 1.5 cm diameter x 4.0 cm length, is connected to the effluent end of the Tenax cartridge to prevent contamination of the cartrige by laboratory vapors. The vegetation sample is cooled to ~4°C. A sample (2 g) is shredded in 200 ml of cold, distilled water in a blender. The mixture is transferred to a 250 ml purge flask and a glass wool plug inserted into the center neck of the flask just above the level of the solution. With the flask in a heating mantle, the solution is heated to 90°C while stirring with a magnetic stirrer. The sample is purged at 25 ml helium/min and 90°C for 90 minutes. The loaded cartridge is removed and stored in a culture tube containing 1-2 g $CaSO_4$ dessicant for at least two hours. The dessicant is removed from the culture tube and the dry, loaded cartridge stored at -5°C.

7.3 Analysis of Sample Purged on Cartridge

The instrumental conditions for the analysis of halogenated hydrocarbons of the sorbent Tenax GC sampling cartridge is shown in Table K1. The thermal desorption chamber and six-port valve are maintained at 270° and 200°C, respectively. The glass jet separatory is maintained at 240°. The mass spectrometer is set to scan the mass range from 25-350. The helium purge gas through the desorption chamber is adjusted to 15-20 ml/min. The nickel capillary trap at the inlet manifold is cooled with liquid nitrogen. In a typical thermal desorption cycle a sampling cartridge is placed in the preheated desorption chamber and helium gas is channeled through the cartridge to purge the vapors into the liquid nitrogen cooled nickel capillary trap. After desorption the six-port valve is rotated and the temperature on the capillary loop is rapidly raised (greater than 10°/min); the carrier gas then introduces the vapors onto the high resolution GLC column. The glass capillary column is temperature programmed from 20°

Table K1. OPERATING PARAMETERS FOR GLC/MS/COMP SYSTEM

Parameter	Setting
Inlet-manifold	
desorption chamber	270°C
valve	220°C
capillary trap - minimum	-195°C
maximum	+180°C
thermal desorption time	4 min
GLC 100 m glass SCOT-OV101	
50 m glass SCOT-Carbowax 20M	20-240°C, 4/C° min
	80-240°C
carrier (He) flow	~3 ml/min
transfer line to ms	240°C
MS	
scan range	*m/e* 20 → 300
scan rate, automatic-cyclic	1 sec/decade
filament current	300 µA
multiplier	6.0
ion source vacuum	~4 x 10^{-6} torr

to 240°C at 4°/min and held at the upper limit for a minimum of 10 min. After all of the components have eluted from the capillary column the analytical column is then cooled to ambient temperature and the next sample is processed (2).

An example of the analysis of volatile organics in ambient air is shown in Figure K3 and the background from a blank cartridge is Figure K4. The high resolution glass capillary column was coated with OV-101 stationary phase which is capable of resolving a multitude of compounds, including halogenated hydrocarbons, to allow their subsequent identification by MS/COMP techniques; in this case over 120 compounds were identified in this chromatogram.

7.3.1 Operation of the MS/COMP System (Figure K5)

Typically the mass spectrometer is first set to operate in the repetitive scanning mode. In this mode the magnetic is automatically scanned exponentially upward from a preset low mass to a high mass value. Although the scan range may be varied depending on the particular sample, typically the range is set from m/e 25 to m/e 300. The scan is completed in approximately three seconds. At this time, the instrument automatically resets itself to the low mass position in preparation for the next scan, and the information is accumulated by an on-line 620/L computer and written onto magnetic tapes of the dual disk system. The reset period requires approximately three seconds. Thus, a continuous scan cycle of six seconds/scan is maintained and repetitively executed throughout the chromatographic run. The result is the accumulation of a continuous series of mass spectra throughout the chromatographic run in sequential fashion.

Prior to running unknown samples the system is calibrated by introducing a standard substance, perfluorokerosene, into the instrument and determining the time of appearance of the known standard peaks in relation to the scanning magnetic field. The calibration curve which is thus generated will be stored in the 620/L computer memory. This calibration serves only to calibrate the mass ion over the mass scanning range.

While the magnet is continuously scanning the sample is injected and the automatic data acquisition is initiated. AS each spectrum is acquired by the computer each peak which exceeds a preset threshold is recognized

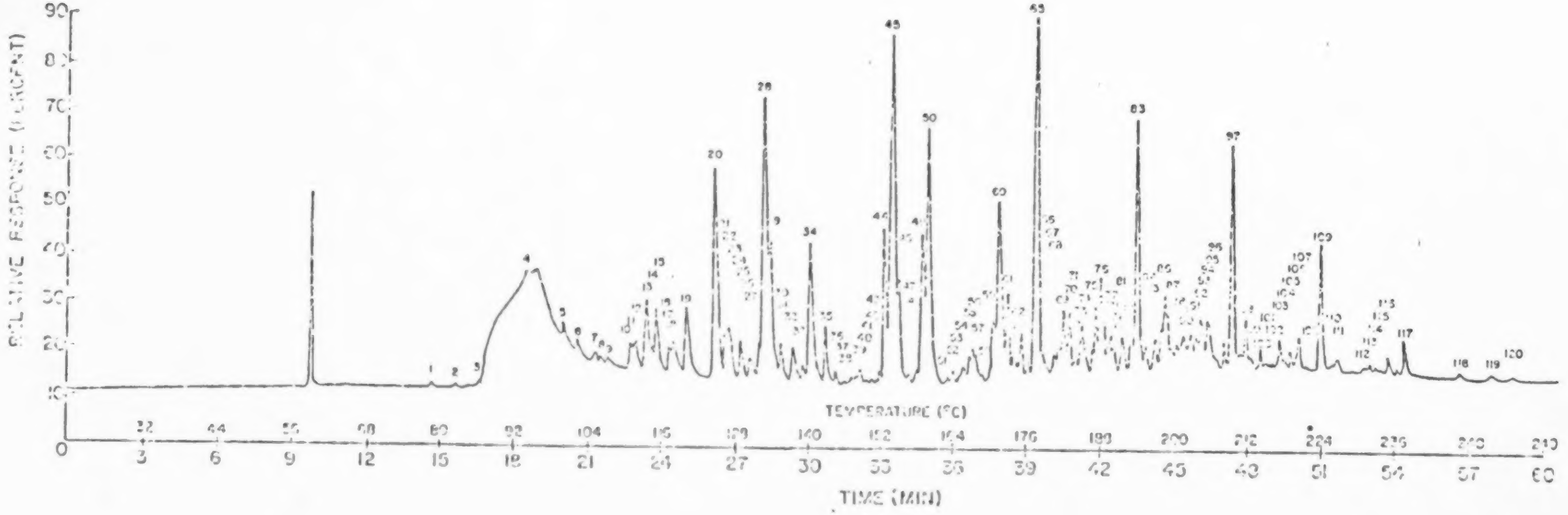

Figure K3. Profile of ambient air pollutants for Wood River, IL using high resolution gas chromatography/mass spectrometry/computer.

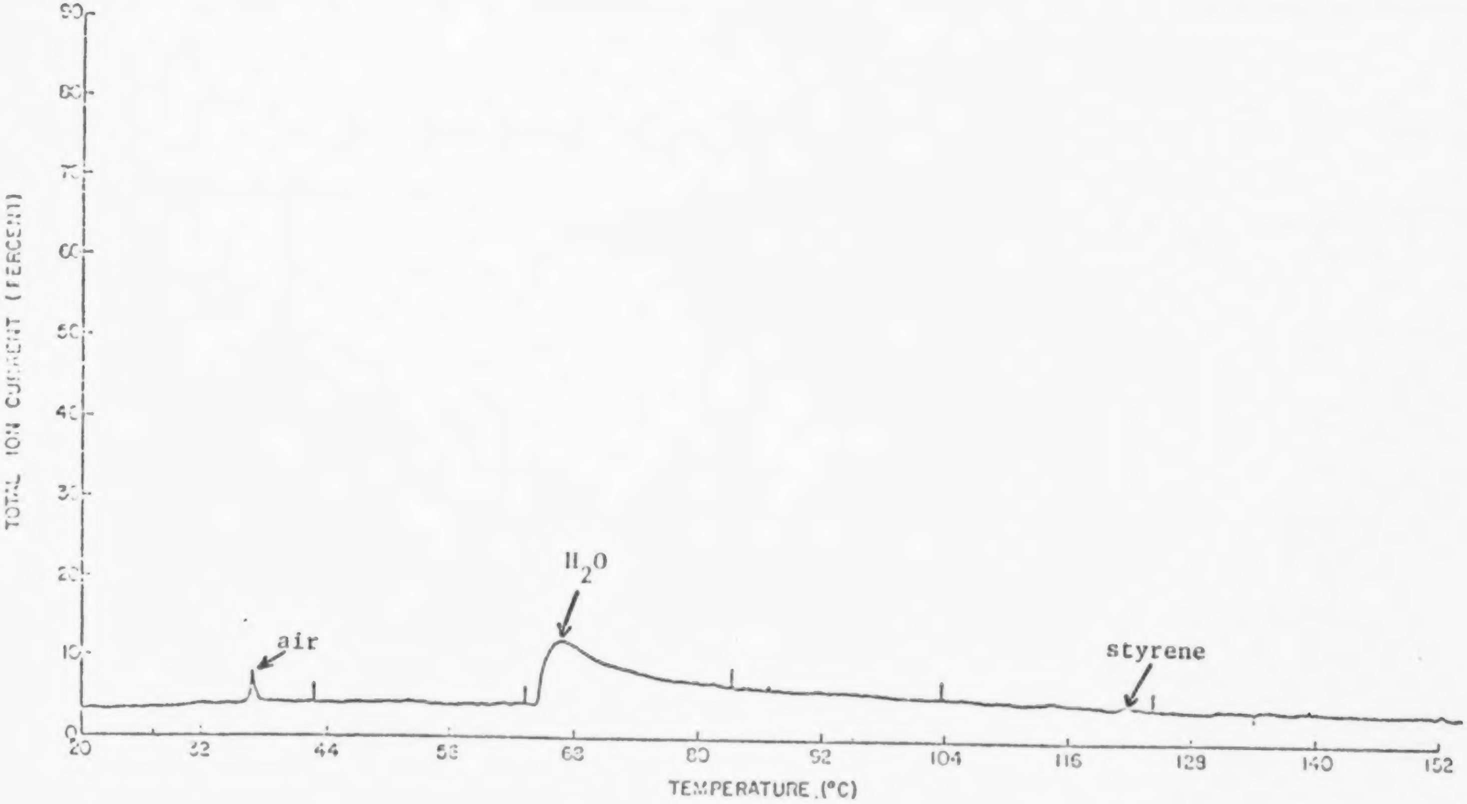

Figure K4. Background profile for Tenax GC cartridge blank.

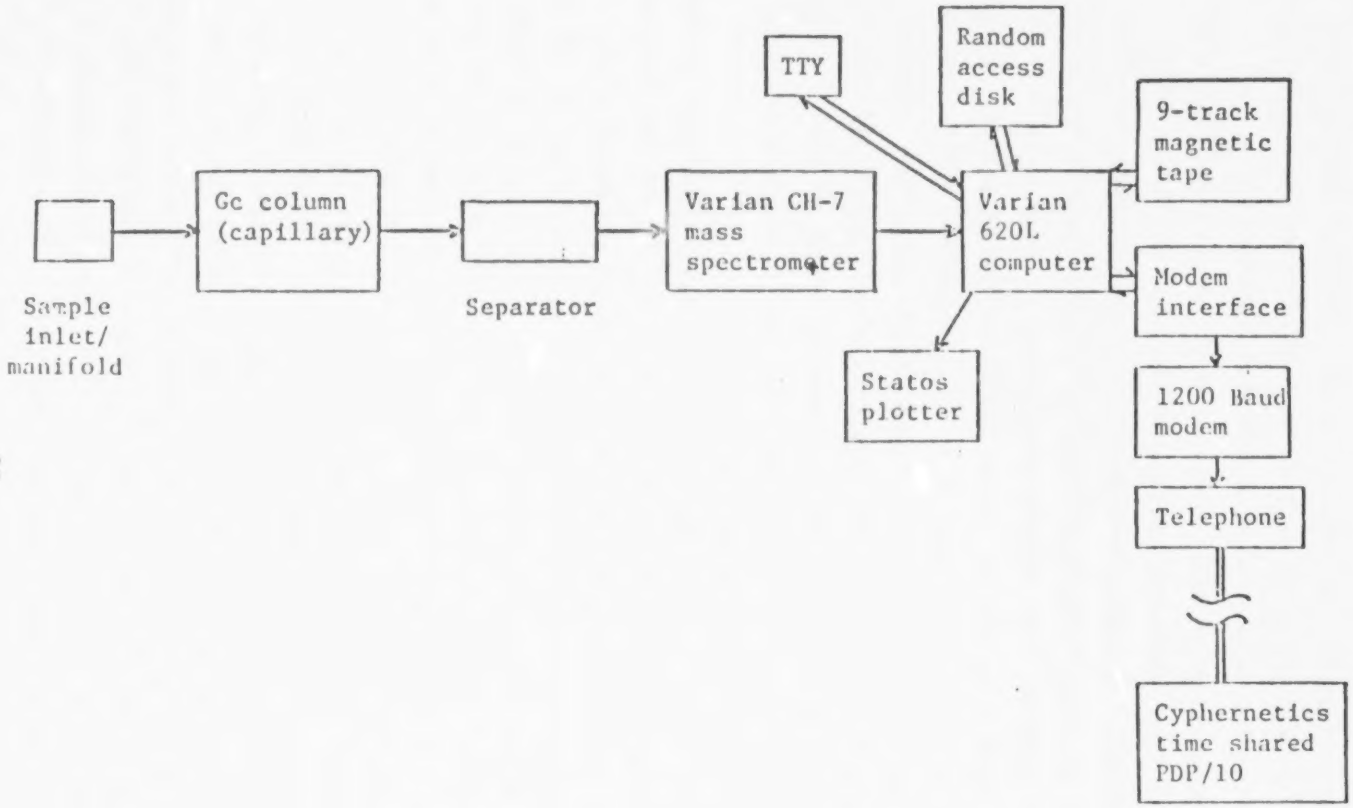
Sample inlet/ manifold
Gc column (capillary)
Separator
Varian CH-7 mass spectrometer
TTY
Random access disk
Varian 620L computer
Statos plotter
9-track magnetic tape
Modem interface
1200 Baud modem
Telephone
Cyphernetics time shared PDP/10

Figure K5. Schematic diagram of gc-ms computer system

and reduced to centroid time and peak intensity. This information is stored in the computer core while the scan is in progress. In addition, approximately 30 total ion current values and an equal number of Hall probe signals are stored in the core of the computer as they are acquired. During the three second period between scans this spectral information, along with the spectrum number, is written sequentially on disks, and the computer is reset for the acquisition of the next spectrum.

This procedure continuous until the entire GC run is completed. By this time there are from 300-1,000 spectra on the disk which are then subsequently processed. Depending on the information required, the data may then either be processed immediately or additional sampels may be run, stored on magnetic tape and the results examined at a later time.

The mass spectral data are processed in the following manner. First, the original spectra are scanned and the total ion current (TIC) information is extracted. Then the TIC intensities are plotted against the spectrum number on the Statos 31 recorder. The information will generally indicate whether the run is suitable for further processing, since it will give some idea of the number of unknowns in the sample and the resolution obtained using the particular GLC column conditions.

The next stage of the processing involves the mass conversion of the spectral peak times to peak masses which is done directly via the dual disk system. The mass conversion is accomplished by use of the calibration table obtained previously using perfluorokerosene. Normally on set of the calibration data is sufficient for an entire day's data processing since the characteristics of the Hall probe are such that the variation in calibration is less than 0.2 atomic mass units/day. A atypical time required for this conversion process for 1,000 spectra is approximately 30 min.

After the spectra re obtained in mass converted form, processing proceeds either manually or by computer. In the manual mode the full spectra of scans from the GC run are recorded on the Statos 31 plotter. The TIC information available at this time is most useful for deciding which spectra are to be analyzed. At the beginning of the runs where peaks are very sharp nearly every spectrum must be inspected individually to determine the identity of the component. Late in the chromatographic run when the peaks are broader only selected scans need to be analyzed.

Identification of resolved components is achieved by comparing the mass cracking patterns of the unknown mass spectra to an eight major peak index of mass spectra (9). Individual difficult unknowns are searched by the use of the Cornell University STIRS and PBM systems. Unknowns are also submitted to the EPA MSSS system for identification. When feasible the identification of unknowns are confirmed by comparing the cracking pattern and elution temperatures for two different chromatographic columns (OV-101 and OV-17 SCOT capillaries) for the unknown and authentic compounds. The relationship between the boiling point of the identified halogenated hydrocarbon and the elution temperature on a non-polar column (the order of elution of constituents is predictable in homologous series since the OV-101 SCOT capillary separates primarily on the basis of boiling points) is carefully considered in making structure assignments.

8.0 Quantitative Analysis

In many cases the estimation of the level of pollutants by capillary gas chromatography in combination with mass spectrometry is not feasible utilizing only the total ion current monitor (see Figure K3 for example), since baseline resolution between peaks is not always achieved. We employ the techniques which have been previously developed under contract whereby full mass spectra are obtained during the chromatographic separation step and then selected ions are presented as mass fragmentograms using computer software programs which allow the possibility of deconvoluting constituents which were not resolved in the total ion current chromatogram (6). Examples are depicted in Figures K6 and K7 which represent an ambient air sample with a TIC profile as in Figure K3.

In our GC/MS/COMP system we request from the Varian 620/L dedicated computer, mass fragmentograms for any combination of m/e ions when full mass spectra are obtained during chromatography. Thus selectivity is obtained by selecting the unique ion for that particular halogenated hydrocarbon, and this is represented versus time with subsequent use of that ion intensity for quantitation. Also, quantitation with external standards is easily achieved using the intensity of the total ion current monitor or the use of a unique mass cracking ion in the mass spectrum of that external standard. Thus, we use mass fragmentography for the quantitation of

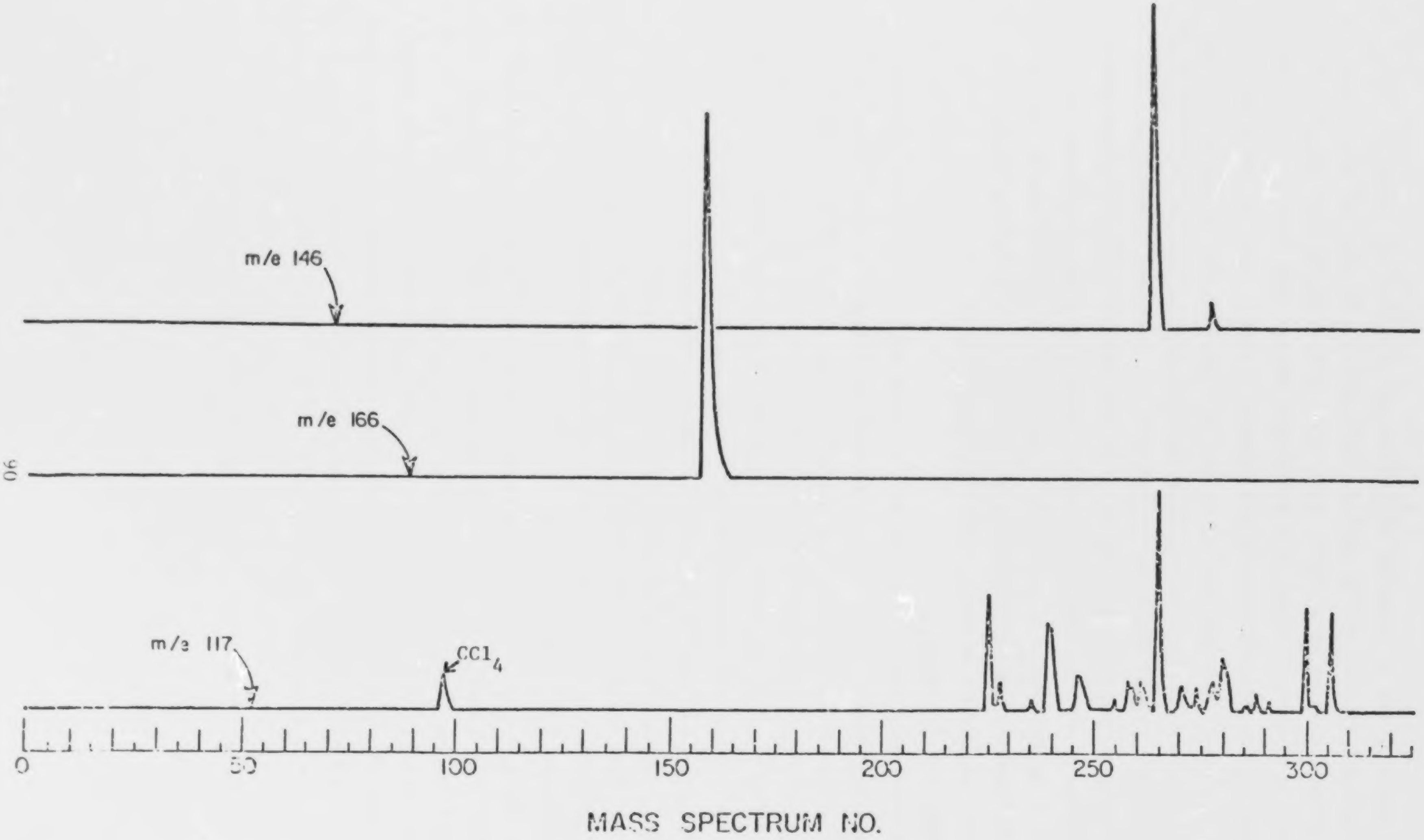

Figure K6. Mass fragmentograms of characteristic ions representing carbon tetrachloride (m/e 117), tetrachloroethylene (m/e 166) and m-dichlorobenzene (m/e 146) in ambient air.

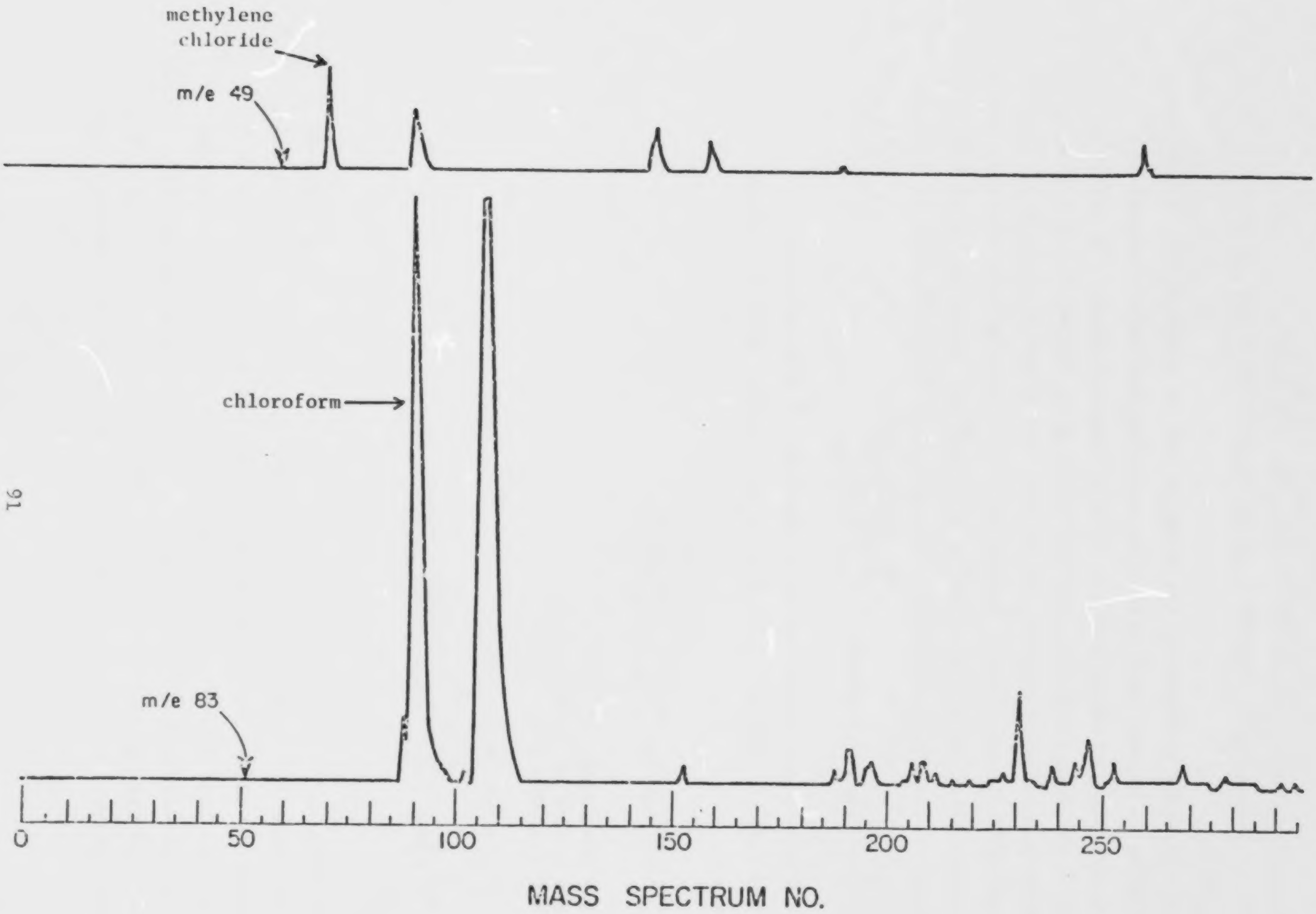

Figure K7. Mass fragmentograms of characteristic ions representing methylene chloride (m/e 49) and chloroform (m/e 83) in ambient air.

halogenated hydrocarbons in ambient air when the total ion current is inadequate because of a lack of complete resolution between components in the mixture.

As described previously, the quantitation of constituents in ambient air samples is accomplished either by utilizing the total ion current monitor or where necessary the use of mass fragmentograms. In order to eliminate the need to obtain complete calibration curves for each compound for which quantitative information is desired, we use the method of relative response (RMR) factors (10). Successful use of this method requires information on the exact amount of standard added and the relationship of RMR (unknown) to the RMR (standards). The method of calculation is as follows:

$$(1)\quad \text{RMR}_{\text{unknown/standard}} = \frac{A_{\text{unk}}/\text{Moles}_{\text{unk}}}{A_{\text{std}}/\text{Moles}_{\text{std}}}$$

A = peak area, determined by integration or triangulation.

The value of RMR was determined from at least three independent analyses.

$$(2)\quad \text{RMR}_{\text{unk/std}} = \frac{A_{\text{unk}}/g_{\text{unk}}/\text{GMW}_{\text{unk}}}{A_{\text{std}}/g_{\text{std}}/\text{GMW}_{\text{std}}}$$

A = peak area, as above
g = number of grams present
GMW = gram molecular weight

Thus, in the sample analyzed:

$$(3)\quad g_{\text{unk}} = \frac{A_{\text{unk}} \cdot \text{GMW}_{\text{unk}} \cdot g_{\text{std}}}{A_{\text{std}} \cdot \text{GMW}_{\text{std}} \cdot \text{RMR}_{\text{unk/std}}}$$

The standard added can be added as an internal standard during sampling. However, since the volume or weight of samples for a given analysis taken is accurately known, it is also possible and more practical to use an external standard whereby the standard is introduced into the cartridge prior to its analysis. Two standards, hexafluorobenzene and perfluorotoluene are used for the purpose of calculating RMR's. From previous research it has been determined that the retention times for these two compounds are such that they elute from the glass capillary column (OV-101) at a temperature and retention time which does not interfere with the analysis of unknown compounds in ambient air samples.

Since the volume or weight of a given sample is accurately known and an external (or internal) standard is added to the sample, then the weight can be determined per cartridge and hence the concentration of the unknown. The approach for quantitating pollutants requires that the RMR is determined for each constituent of interest. This means that when sample is taken, the external standard is added during the analysis at a known concentration. It is not imperative at this point to know what the RMR of each of the unknown constituents. As the RMR may be determined subsequently and the concentration calculated in the original sample using the RMR. In this manner it is possible to obtain qualitative and quantitative information on the same sample with a minimum of effort.

9.0 Calculations

The g_{unk} determined by the RMR technique can be related to the original sample concentration as follows:

Water and milk

$$\mu g \text{ halogenated hydrocarbon}/\ell = \frac{g_{unk} \times 10^6}{\text{aliquot taken } (\ell) \times \text{purge recovery}}$$

Soil, Sediment, Vegetaticn

$$\mu g \text{ halogenated hydrocarbon/kg} = \frac{g_{unk} \times 10^6}{\text{aliquot taken (kg)} \times \text{purge recovery}}$$

Purge recoveries for several compounds and media are given in Table K2.

10.0 References

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2. Pellizzari, E. D., Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. Publication No. EPA-600/2-76-076, Contract No. 68-02-1228, 185 pp., November, 1975.
3. Pellizzari, E. D., J. E. Bunch, B. H. Carpenter and E. Sawicki, Environ. Sci. Tech., 9, 552 (1975).

Table K2. RECOVERY STUDIES - VOA METHOD

Compound	Amount Spiked (µg)	Medium	Amount Recovered (µg) 1	2	3	Average % Recovery	S.D.
1-chloro-1-butene	0.926	dist. H_2O	0.710	0.743	Data Not Included; Instrumental Error	78.5	0.0233
1,2-dichloroethane	0.853	dist. H_2O	0.739	0.654		81.6	0.0601
1-bromo-2-chloroethane	1.137	dist. H_2O	0.922	0.913		80.7	0.00636
1,2-dibromoethane	2.253	dist. H_2O	1.839	1.655		77.5	0.130
bromobenzene	1.663	dist. H_2O	1.435	1.927		101.8	0.347
m-chlorotoluene	1.400	dist. H_2O	1.355	1.358		96.9	0.00212
1-chloro-1-butene	0.880	stream H_2O	0.651	0.628	0.554	69.4	0.0507
1,2-dichloroethane	0.810	stream H_2O	0.593	0.556	0.255	57.8	0.185
1-bromo-2-chloroethane	1.080	stream H_2O	1.041	1.022	1.099	96.6	0.0401
1,2-dibromoethane	2.140	stream H_2O	1.969	1.850	2.643	100.7	0.428
bromobenzene	1.580	stream H_2O	1.657	1.326	1.810	101.1	0.247
m-chlorotoluene	1.330	stream H_2O	1.337	0.999	1.074	85.5	0.178
1-chloro-1-butene	0.880	soil	0.266	0.238	0.392	33.9	0.0820
1,2-dichloroethane	0.810	soil	0.436	0.481	0.611	62.9	0.0909
1-bromo-2-chloroethane	1.080	soil	0.679	0.625	0.978	70.4	0.190
1,2-dibromoethane	2.140	soil	1.471	1.600	1.922	77.8	0.232
bromobenzene	1.580	soil	0.968	1.254	1.417	76.8	0.227
m-chlorotoluene	1.330	soil	0.881	0.830	1.134	71.3	0.163

4. Pellizzari, E. D., B. H. Carpenter, J. E. Bunch and E. Sawicki, Environ. Sci. Tech., 9, 556 (1975).

5. Pellizzari, E. D., Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors, 1976, in preparation.

6. Pellizzari, E. D., J. E. Bunch, R. E. Berkley and J. McRae, Anal. Chem., 48, 803 (1976).

7. Pellizzari, E. D., Quarterly Report No. 1, EPA Contract No. 68-02-2262, February, 1976.

8. Pellizzari, E. D., J. E. Bunch, R. E. Berkley and J. McRae, Anal. Lett., 9, 45 (1976).

9. "Eight Peak Index of Mass Spectra", Vol. L (Tables 1 and 2) and Vol. II (Table 3), Mass Spectrometry Data Centre, AWRE, Aldermaston, Reading, RF74PR, UF, 1970.

10. Pellizzari, E. D., Quarterly Report No. 3, EPA Contract No. 68-02-2262, in preparation.

L. SAMPLING AND ANALYSIS OF SEMI-VOLATILE HALOGENATED HYDROCARBONS IN AIR, SOIL, SEDIMENT, WATER AND BIOTA

1.0 Principle of the Method

Air-borne particulate are collected on glass fiber filters using Hi-Vol samplers. The glass fiber filter is then subjected to solvent extraction and analyzed by one of several gc or thin-layer techniques. Other media such as soil, sediment, water and biota are solvent extracted and with the exception of biota which is submitted directly to the analytical technique of choice. The analytical technique is a function of compound to be analyzed. Techniques were developed specifically for TRIS, Decabrom, Tetrabrom, Firemaster 680 and brominated phenols. All of these compounds can be analyzed by gc/ms with multiple ion detection, however, substantially better limits of detection for TRIS are obtained using glc/ecd for its analysis. Some biota samples such as milk are purified using gel permeation before gc/ms analysis. Thin-layer chromatography is also used for the analysis of TRIS and Decabrom.

2.0 Range and Sensitivity

The range and sensitivity of an analysis for semi-volatile halogenated compounds depends upon the specific compound and the matrix from which it is derived. Table L1 indicates these parameters for the five example compounds. Biota samples such as milk, hair, and placenta are very special cases since they require additional purification for analysis. The high lipid content of these samples reduces the sensitivity of any of the analytical methods to approximately 0.1 μg/g or higher depending upon the sensitivity of the instrumental method to that particular compounds.

3.0 Interferences

The extent of interference with the gc/ms detection of these compounds is a function of the molecular weight and principle ions of the compound under investigation. For compounds such as Decabrom where the molecular weight is very high and unique isotope clusters are clearly evident, there is very little problem with interference, however, for a compound such as Firemaster 680 where the parent ion cluster is relatively weak and a lower molecular weight must be monitored for low detection limits interferences become more pronounced. The very low sensitivity of the quadrupole mass

Table L1. **DETECTION LIMITS FOR SELECTED SEMIVOLATILE HALOGENATED ORGANICS.**

Compound	Matrix			
	Air ng/m^3	Water µg/ℓ	Sediment µg/Kg	Soil µg/Kg
TRIS	614^a	$500\text{-}1000^a$	5000-10,000	$1000 - 2000^a$
	4^b	0.2^b	5	1^b
	250^c	20^c		
Decabrom	$20 - 100^a$	10^a	100^a	20^a
		2.5^c	50^e	10^c
Tetrabrom	10^a	50^a	500^a	100^a
Firemaster 680	10^a	50^a	500^a	100^a
Pentabromophenol	25^a	100^a	1000^a	200^a

a. GC/MS/COMP analysis - Range ~ 10^3.
b. GC/ECD analysis - Range 10-50.
c. TLC/SD analysis - Range 10.

spectrometer to TRIS is further complicated by the fact that the principle ions are quite common. No apparent background has been observed using the gc/ecd method for TRIS. Tetrabrom and pentabromophenol are less subject to interference than Firemaster 680 due to their early elution time and relatively high molecular ion. The thin-layer procedure for Decabrom is subject to some interference and in particular with the soil extracts. This particular aspect is the most serious limitation of that approach to analyzing Decabrom. There is one additional problem with the thin-layer procedure and that is lack of resolution between Decabrom and polybrominated biphenols. The thin-layer feature developed for the analysis of TRIS is subject to interference from other brominated compound but non-brominated compounds present little interference in this method.

4.0 Precision and Accuracy

For the glc/ms/comp analysis, an estimation of the precision of the analytical method may be assessed by the standard deviation of response factors generated from standard samples. Over a nine-day period, 21 separate determinations of the five selected compound yielded at relative standard deviation of 24%. Actual results are somewhat better than this since there is day-to-day variation in the instrument response. By running calibration standards on a daily basis, this element of variation is removed.

Estimation of accuracy is based upon knowledge of the range of recoveries and instrumental accuracy. The standardization of the gc/ms/comp system was based on three sets of standard mixtures at varying relative concentration to the internal standard. The variability between these was no larger than day-to-day instrumental sensitivity and variations. The recoveries from each of the matrices analyzed were determined for some of these compounds. These recoveries are summarized in Table L2. With the exception of EDB in soil, the recoveries were generally 80% or better than 100%.

5.0 Apparatus

5.1 Sampling Apparatus

5.1.1 Air

General Metals Works Model GMWL-2000

High Volume Air Sampling System or equivalent

Table L2. RECOVERIES OF BROMINATED ORGANICS FROM SEVERAL MATRICES BY SOLVENT EXTRACTION

Compound	Matrix					
	Air		Water		Soil	
	Amt. Added	% Recovered	Amt. Added	% Recovered	Amt. Added	% Recovered
TRIS	104 ng/cm^2	87%[a]	100 µg/ℓ	101 ± 20[a]	100 µg/Kg	77%[a]
	(27 ng/m^3)				1000 µg/Kg	81%[a]
	1110 ng/cm^2	91%[a]				
	(286 ng/m^3)					
Decabrom	48 ng/cm^2	TRACE[bc]			100 µg/Kg	84%[b]
	(16 ng/m^3)				100 µg/Kg	110%[d]
					1000 µg/Kg	85%[b]
	512 ng/cm^2	100 ± 20[b]				
	(170 ng/m^3)					
Tetrabrom					100 µg/Kg	162%[c]
EDB	--	--	10 µg/ℓ	87 + 6[ae]	1000 µg/Kg	52%[a]

a. Analysis by GC/ECD.
b. Analysis by TLC/SD.
c. Below the limit of quantitation.
d. Analysis by GC/MS/COMP. These samples were at or near the limit of detection.
e. Hexane extraction.

5.1.2 Water, Sediment, Soil and Biota

Garden bulb planter

Dipper for obtaining water samples in remote places

5.2 Sample Extraction And Purification

5.2.1 Air

Ultrasonic bath or reciprocal shaker

5.2.2 Water, Sediment and Soil

Reciprocal shaker

Separatory Funnels (250 ml)

Kuderna-Danish Evaporators

5.2.3 Biota

Centrifuge (clinical)

Kuderna-Danish Evaporators (micro)

Virtis homogenizer or equivalent Soxhlet evaporator (250 ml capacity)

High Pressure Liquid Chromatograph with variable wavelength uv detector, refractive index desirable but not essential.

Gel permeation column: μStyragel, 500 Å 27 cm in length.

5.3 Extract Analysis

5.3.1 GC/MS/COMP Analysis

GC/MS/COMP system capable of operating in the multiple ion detection mode GC columns 0.2 cm i.d. x 42 cm packed with 2% OV-101 on Chromosorb W(HP) [100/120 mesh].

5.3.2 GC/ECD Analysis

Gas chromatograph with electron capture detector (on column injection).

Columns:

1. 0.2 cm i.d. x 42 cm glass column packed with 2% SE-30 on Chromosorb W(HP) (80/100 mesh)
2. 0.2 cm i.d. x 42 cm glass column packed with 3% OV-17/0.5%. Benzyltriphenyl phosphonium chloride (BTPP Cl) Chromsorb W(HP) [100/120 mesh].

3. 0.2 cm i.d. x 170 cm glass column packed with 3% Carbowax 20M on Chrom G AW/DMCS (100/120 mesh).

4. 0.2 cm i.d. x 42 cm glass column packed with 2% OV-101 on Gas Chrom Q (100/120 mesh).

5.3.3 TLC/SD Analysis

Developing Chambers

Spotting Apparatus

Scanning densitometer *e.g.* the Schoeffel SD3000 Spectrodensitometer

6.0 Materials

Authentic samples of the compounds under analysis.

6.1 Sampling

6.1.1 Air

Gelman Type A glass fiber filters 20 x 25 cm

Aluminum Foil

Ziphok® bags

Mailing Tuber

6.1.2 Water

Narrow mouth 1 ℓ amber glass bottles with foil-lined caps.

6.1.3 Soil and Sediment

Wide mouth 1 ℓ glass bottles with foil-lined caps.

6.1.4 Biota

Tedlar® bags 36 x 36 cm (milk)

Wide mouth 500 ml glass bottles (placenta)

Wide mouth 1 ℓ glass bottles (hair)

6.2 Sample Extraction

Separatory funnels (250 mℓ)

Graduated cylinders (100 and 240 mℓ)

1 ℓ glass bottles

500 ml round bottom flasks

Other general glassware

Solvents - Toluene, hexane, ethyl ether, acetone (redistilled or "distilled in glass")

6.3 Analytical Procedures

Carrier Gases

Solvents for TLC

7.0 Procedure

7.1 Collection of Samples

7.1.1 Air

Locate a suitable power source for the Hi-Vol sampler. Place a glass fiber filter in the holder making sure there are no holes in it. Turn on the sampler and observe the flow rate. If the flow rate is normal for that sampler (40-60 cfm) record the time and flow rate and continue sampling for 24 hrs. Lower the roof of the shelter to protect from rain, etc. At the end of the sampling period, observe and record the time and flow rate. Turn off and remove the filter folding the sample sides together. Wrap the folded filter in foil, label and roll into a shape which will fit in a mailing tube.

7.1.2 Soil

Soil samples are collected by taking cores with a garden bulb planter. The cores are placed in one liter wide mouth jars and sealed with foil lined caps. The sample is labeled and its location and other pertinent data recorded on a protocol sheet.

7.1.3 Water and Sediment

Water samples are 1 ℓ grab samples acquired by filling 1 ℓ amber narrow mouth bottles by immersion or ladeling depending upon accessibility. Sediment samples are obtained by coring where the sediment is firm or by scooping if coring is not possible.

7.1.4 Hair and Placenta

Hair samples are composited at the site in a wide mouth 1 ℓ bottle. With the cooperation of the barber, the number of individuals contributing to the composite is recorded as the sample is added to the jar. A well filled 1 ℓ bottle will contain approximately 15 g of hair.

Placenta and cord samples are obtained by supplying an attending physician with 500 ml or 1 ℓ wide mouth bottles. Collected samples must be refrigerated or preferably frozen.

7.1.5 Milk

Milk is collected in 1 ℓ wide mouth bottles and transferred to 1 ℓ Tedlar® bags before being frozen.

8.0 Extraction and Purification

8.1 Air Samples

The glass fiber filter samples are carefully cut into 4 x 10 cm segments taken from the central area of the filter. The segments are then further cut into narrow strips (~5 mm wide). These are placed in 20 ml vials along with 10 ml acetone and sonicated in an ultrasonic bath for 30 min. The extraction can also be accomplished on a reciprocal shaker at ~120 cpm for 2 hrs. An aliquot of the supernatant is drawn off for analysis.

8.2 Water Samples

Two parallel extractions are performed, one, a hexane extraction, for a volatile fraction such as ethylene dibromide (EDB), and the other, a toluene extraction, for more polar, less volatile compounds such as decabromobiphenyl ether and TRIS.

8.2.1 Hexane Extraction of Water

An aliquot of 100 ml of sample is placed in a 250 ml separatory funnel. Hexane (10 ml) is added, the funnel stoppered and shaken for 30 minutes. The phases are allowed to separate for at least 5 minutes. The aqueous layer is drained into another separatory funnel and the hexane into a 50 ml Erlenmeyer flask. Repeat the hexane extraction above two additional times combining the hexane extracts. Dry the hexane extract over Na_2SO_4. The extract may be analyzed directly by GC/ECD or the volume reduced to 5 ml in the K-D apparatus for other analyses.

8.2.2 Toluene Extraction of Water

An aliquot of sample (200 ml) is placed in a 250 ml separatory funnel and 20 ml of toluene added. The funnel is shaken for 30 minutes and then allowed to stand for 5 minutes for the phases to separate. The aqueous layer is drained into another separatory funnel and the toluene into a 100 ml Erlenmeyer flask. The toluene extraction is repeated two additional times combining the extracts. The extracts are dried over Na_2SO_4, transferred to a round bottom flask (500 ml) with 5-10 ml toluene wash and evaporated using a Snyder column to a final volume of 5 ml. All procedures are carried out under minimum lighting and samples are stored in the dark at 5°C.

8.3 Soil and Sediment Samples

Composite 1/2 of top 2.5 cm of soil core and place in 1 ℓ wide mouth jar with other samples to be composited and cap with foil-lined cap. Agitate vigorously to produce a homogeneous sample. A 50 g portion of the composite is then extracted in a 1 ℓ wide mouth jar with 50 ml of diether ether (shake for 30 minutes). Decant the ether extract through glass wool into a Kuderna-Danish (K-D) apparatus and combine with subsequent extracts.

The soil residue is then treated with acetone (40 ml) and shaken for 20 minutes. Toluene (80 ml) is added and shaken for 10 minutes. The extract is decanted through a glass wool plug into a 500 ml round bottom flask. The above acetone-toluene extraction is repeated a total of 2 times and the extracts concentrated by heating the round bottom flask with a 3 ball Synder column attached. The final volume was adjusted to 5 ml. All procedures are conducted under minimum light and samples are stored in the dark at 5°C. These extracts are used in several analytical methods described below.

8.4 Milk Samples

8.4.1 Extraction

Weigh a 10 g sample of well mixed milk. Mix with clean glass wool and precipitate the proteins by adding 100 ml of acetone. Centrifuge if necessary to facilitate separation. The acetone is removed and filtered as are two additional 25 ml acetone washes. The volume of the acetone is reduced to ~20 ml using a Snyder column. Wash the remaining precipitate with 2 portions of toluene (10 ml each). The toluene and acetone fractions are combined. The resulting two phases are separated and the aqueous phase discarded. The organic phase is dried over sodium sulfate and the volume reduced to ~5 ml.

8.4.2 Purification

In order to remove the bulk of the butterfat from the extract gel permeation chromatography is used. Using toluene as a solvent establish the retention time/volume of the compounds of interest especially the highest molecular weight compound Decabrom. Using blank milk extract determines the profile of the butterfat in the extract These retention volumes may vary somewhat from column to column and even in time if column efficiency changes. The instrument and column are described under 5.2.3. The absorbance is monitored at 300 nM to avoid the solvent cutoff at ~290 nm. Refractive index is very useful especially for compounds such as TRIS which have no uv absorbance. Once chromatographic performance has been established samples containing octachloronaphthalene internal standard chromatographed using as large an injection as is compatible with resolution (~0.5 ml). Collect the effluent starting before the earliest eluting compound (Decabrom) and continuing past the last compound (Tetrabrom). Repeated injections are made until sufficient material has been collected for analysis. The fractions are combined and the volume reduced for analysis.

8.5 Hair Samples

Weighed samples (~15 g) were soxhlet extracted with toluene for 16 hrs and the volume reduced to 5-10 ml using a Snyder column to avoid losses. Aliquots (0.5 ml) were evaporated to dryness and weight to determine as an internal standard. These aliquots were redissolved and purified using high performance liquid chromatography on a μStyragel (500Å) column with toluene as a solvent. Prior to sample analysis the elution volumes of several marker compounds were established (Decabrom and Firemaster 680) and these elution vaolumes were used to select the fraction collected. Two injections of 50 to 100 μl of extract (~4-8 mg of hair oil) were made of each sample. The fractions from each sample were combined and the volume reduced for submission to GC/MS/COMP analysis. The sample GLC/MS analysis conditions were used as for the soil and sediment samples.

8.6 Placenta Samples

Weighed samples of tissue (~10 g) were homogenized with 100 ml of acetone using a Virtis blender. Otherwise the procedure for extraction was the same as for milk (see 8.4.1). HPLC clean-up is not useful with these samples.

9.0 Instrumental Analysis

9.1 GC/ECD

Gas chromatography-electron capture was used for the determination of TRIS and for screening of other compounds. Two columns were used for TRIS, SE-30 and OV-17 (see section 5.3.2). These columns were also applicable to other compounds such as Tetrabrom, Firemaster 680 and Bromophenols. The temperature of the column and injector must be optimized for each compound, however this optimization is extremely important for TRIS. TRIS is subject to thermal degradation hence the lowest possible injection temperature, on column injection and minimum column temperature are required. Typical chromatograms are shown in Figures L1 and L2 with the conditions. Since the SE-30 column may be operated at a lower temperature, it is the column of choice. Both ^{63}Ni and ^{3}H detectors have been used successfully in detecting TRIS. The detection limit is used not to the detector sensitivity but to column losses.

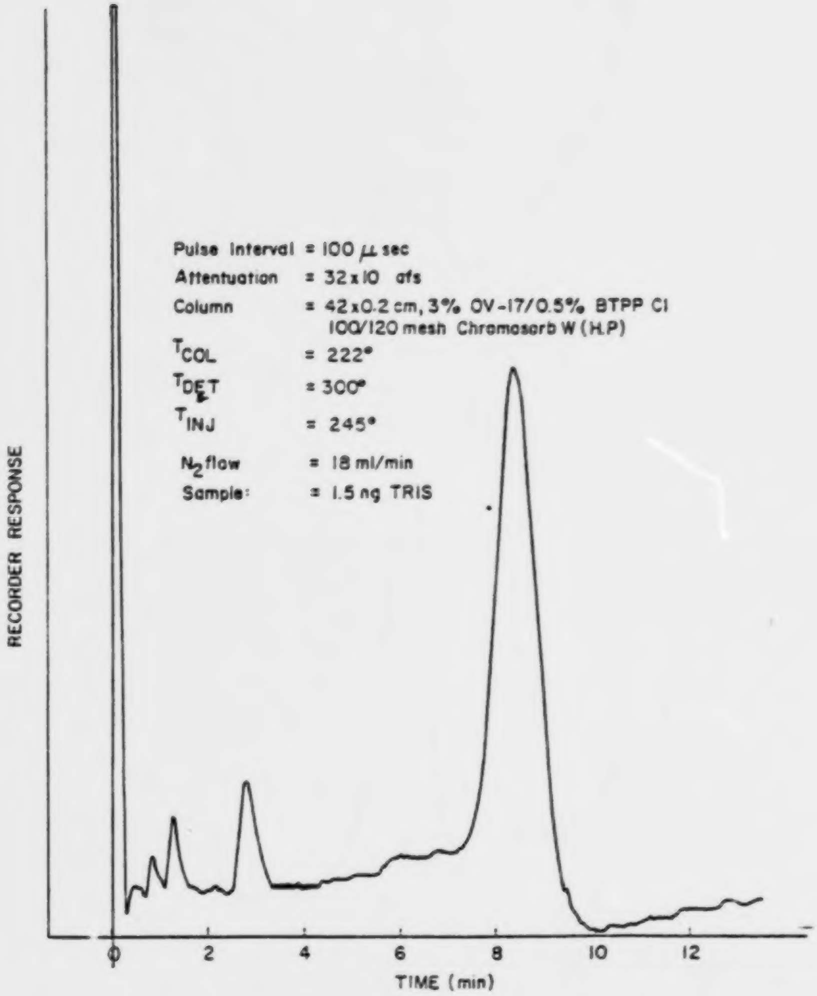
Hexane extracts of water samples are screened for the possible presence of EDB and DBC using the Carbowax 20M column (see 5.3.2) and ECD. For EDB, the column temperature is 90°C, injector 110°C and for DBC 160° and 180°, respectively.

9.2 GC/MS/COMP

9.2.1 Instrumentation - Finnigan 3300 GC/MS with PDP/12 Computer

The Finnigan 3300 mass spectrometer has a mass range of 1000, with unit resolution over the entire range. Calibration of the system is routinely performed with PC-43 for lower mass ranges and tris(perfluoroheptyl)-a-triazine in the higher ranges.

The PDP/12 computer is on-line with the Finnigan system. Long term storage of data is on LINC tapes or removable disc packs. The computer can subsequently treat sotred data in several different ways to facilitate interpretation: (a) a reconstructed gas chromatogram is routinely made to obtain retention times; scan number for a given gas chromatographic peak is obtained by operator interaction with a CRT display; (b) any given mass spectrum or an entire series of scans are corrected for background signal (column bleed, septum bleed, etc.); (c) plots of intensities of specific ions (mass fragmentography) are made from the scan data. This type of information is often useful, when correlated with retention time data, for simplifying the identification of particular compounds. Peak areas are also readily obtainable from these mass chromatograms and can be used to provide quantitative information; (d) normalized mass spectra are plotted, using different types of normalization or amplification factors in order to facilitate identification; (e) hard copy output of normalized data in



Pulse Interval = 100 μ sec
Attentuation = 32 x 10 afs
Column = 42 x 0.2 cm, 3% OV-17/0.5% BTPP Cl
100/120 mesh Chromosorb W (H.P)
T_{COL} = 222°
T_{DET} = 300°
T_{INJ} = 245°
N_2 flow = 18 ml/min
Sample: = 1.5 ng TRIS

GAS CHROMATOGRAM (^{63}Ni ECD) of TRIS

Figure L1. Gas chromatogram (^{63}NI electron capture detection) of tris(2,3-dibromopropyl)phosphate standard.

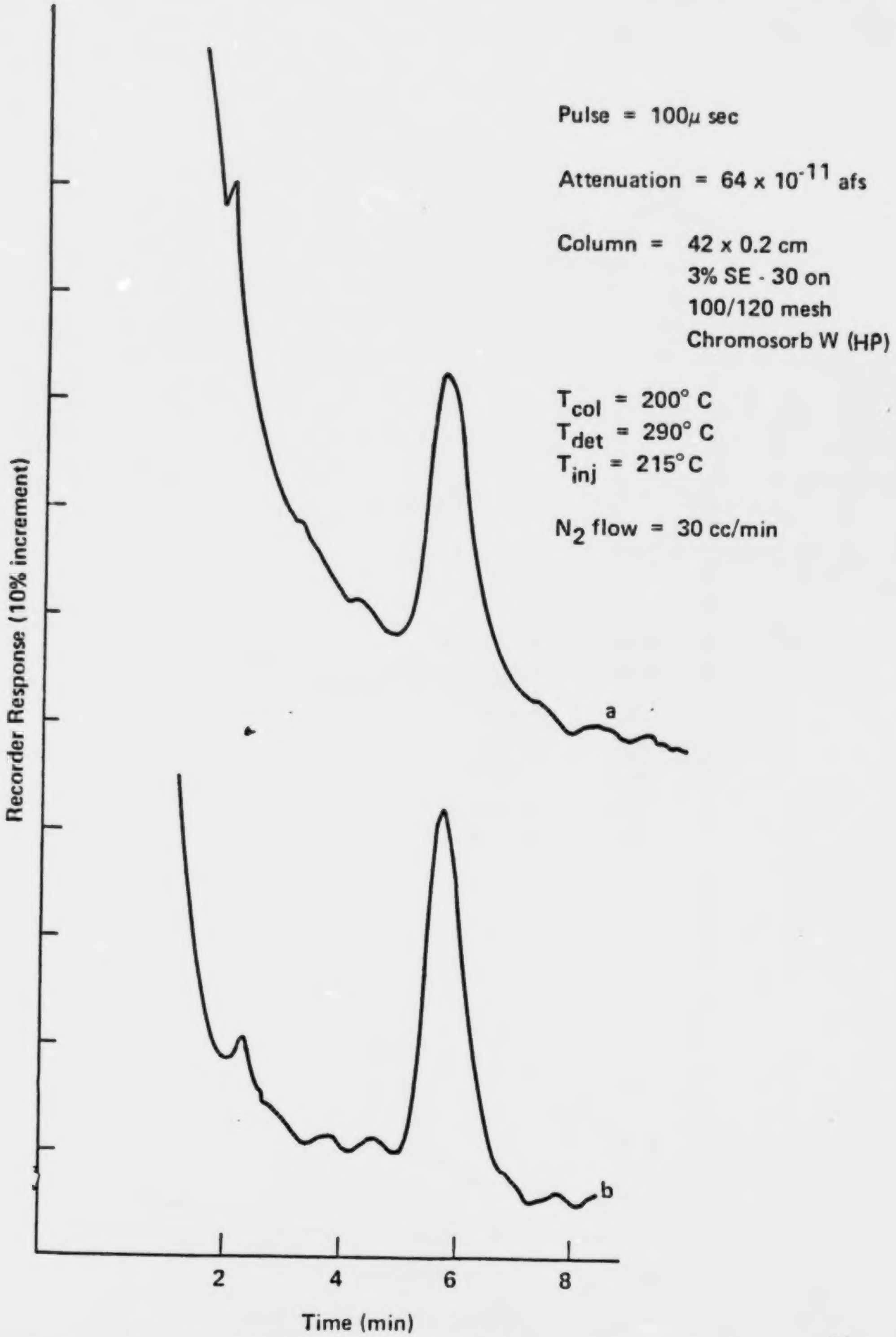


Figure L2. Gas liquid chromatography/electron capture detection (^{63}Ni) of (a) an acetone extract of the Hi-Vol glass fiber filter sample collected 12/22/76 - 12/23/76 at Michigan Chemical Corp., El Dorado, AK and, (b) a TRIS standard (0.8 ng).

digital form, with various forms of background correction, is also available.

The GC system in use on the Finnigan mass spectrometer is a Finnigan 9500.

The basic hardware of the PDP/12 consists of an 8K central processor fitted with a teletype, random access disc, CRT display and electrostatic printer/plotter. The interface to the mass spectrometer was custom-designed and built and consists of both analog to digital as well as ditital to analog interfaces. The latter involves several unique concepts in interface design, since by using this system it is possible to put the entire mass spectral scanning operation under computer control. Since the data acquisition phase of the spectrometer operation is controlled entirely by the computer, a large number of different types of acquisition protocols have been implemented. For example, in the multiple ion detection mode, up to nine individual peaks can be selected within the entire mass spectral range, and acquired for varying time intervals as selected by the operator. In the repetitive scanning mode, scna intervals down to one scan per second are possible with entire scans recorded either on LINC tapes or disc.

All data processing operations are carried out interactively by mans of programs stored on the small computer.

9.2.2 Operating Parameters for Multiple Ion Detection - Screening and Quantitation

In order to obtain compact peak of late eluting compounds such as Decabrom and avoid decomposition of TRIS a short column was utilized. The column, 45 cm x 0.2 cm i.d. glass column packed with 2% OV-101 on Gas-Chrom Q was temperature programmed from 220°C to 300° at 12°/min. Table L3 lists the compounds, the ions and the retention times for each. The samples are run using the "First" ions and as many of the "second" ions as possible. If ions are found having the correct retention time and ratio of intensities where more than one ion for a given compound is monitored, further analyses are performed. If sufficient material is present, the sample is analyzed in the full scan mode to confirm the identity of the brominated compound. If too little of the compound(s) is present, then additional MID analyses are performed selecting additional ions and comparing their intensity ratios with those of authentic compounds.

Table L3. MID IONS SELECTED FOR EACH SEMI-VOLATILE BROMINATED COMPOUND

Compound	Retention Time (min)	Ions Monitored		
		First[a] (m/e)	Second (m/e)	Third (m/e)
Octachloronaphthalene (External standard)	1.4	404		
Pentabromophenol	0.7	488	490	
Tetrabrom	2.2	529	531	
TRIS	2.1	417	419	
Firemaster 680	3.5	357	688	690
Decabrom	7.1	800	802	804

[a] For screening purposes, the ions in the first column plus three from the second were run.

Quantitation was achieved by comparing the computer-calculated integrated area of the brominated compound with the integrated response for a known amount of octachloronaphthalene. To compensate for differences in ionization cross-section, the relative molar response of authentic compounds was obtained.

The calculation of the relative molar response (RMR) factor allows the estimation of the levels of sample components without establishing a calibration curve. The RMR is calculated as the integrated peak area of a known amount of the compound, A°_{unk}, with respect to the integrated peak area of a known amount of standard, A°_{std} (in this case octachloronaphthalene), according to the equation

$$R = \frac{A^{\circ}{}_{unk}/\text{moles}_{unk}}{A^{\circ}{}_{std}/\text{moles}_{std}} = \frac{(A^{\circ}{}_{unk})\ (ms_{unk})\ (g_{std})}{(A^{\circ}{}_{std})\ (mw_{std})\ (g_{unk})} \qquad \text{(Eq. 1)}$$

From this calculated value, the concentration of an identified compound in a sample is calculated by rearranging Equation 1 to give

$$g_{unk} = \frac{(A_{unk})\ (ms_{unk})\ (g_{std})}{(A_{std})\ (mw_{std})\ (\text{RMR})} \qquad \text{(Eq. 2)}$$

The use of RMR for quantitation by GC/MS has been successful in repeated applications to similar research problems.

The RMR's for the compounds were calculated from the numerical integrations of peaks observed in the appropriate MID channel. Typical RMR's listed in Table L4 are mean values of three injections of each of three replicate standard mixtures.

The RMR's given here are to be regarded as typical values not only must they be determined for each instrument, but day-to-day variations are sometimes large enough to require daily calibration. This is particularly true of the higher masses e.g. Decabrom.

Table L4. TYPICAL RMR[a] VALUES FOR SEMI-VOLATILE BROMINATED ORGANICS

Compound	Ion m/e	RMR	S.D.	Ion m/e	RMR	S.D.
Pentabromophenol	488	0.142	0.039	490	0.141	0.036
Tetrabrom	529	0.410	0.066	531	0.279	0.048
Firemaster 680	357	0.752	0.114	688	0.0384	0.0126[b]
Decabrom	800	0.244	0.118	802	0.0494	0.0110[b]

[a] RMR's relative to the OCN 404 ion.

[b] Average of 2 determinations.

9.3 Thin-Layer Chromatography

9.3.1 Decabrom

Samples and standards are spotted in alternate channels of 20 x 20 cm scored silica gel G-plates (Brinkman F_{254}). The plate is developed in 10% toluene:90% hexane. After air drying the plate is can on Schoeffel scanning densitometer in the reflectance mode. The excitation is optimal at 240 nm with unfiltered emission. Examples of standards of Decabrom are shown in Figure L3. Quantitation is obtained by comparing unknowns to standards on the same plate. Linearity is obtained from 50 to 1000 ng/channel with a correlation coefficient of 0.996.

9.3.2 TRIS by TLC

Silica gel TLC plates (20 x 20 cm) are prepared by immersing in a solution of 0.033% fluorescein (acid) in ethanol/acetone 2:1. The plates are air dried and scored in 1 cm channels. Samples and standards are spotted in alternate channels and the plate developed in methylene dichloride. The plates are air dried before spraying liberally with a 1:1 mixture of glacial acetic acid/30% hydrogen peroxide. The plate is then heated at ~100°C in the hood. The spray and heat operations were repeated. Rose-pink spots are visible where >1 μg of TRIS is present. The plate is then scanned on a Schoeffel scanning spectrodensitometer with emission at 520 nm and exictation at 380 nM. The spots appear as quenching of the fluorescein fluorescence. Figure L4 shows examples of chromatograms obtained in this manner. Quantitation is obtained by comparing peak areas of unknowns to standards on the same plate. Linearity extends from 0.2 to 5 μg TRIS per spot.

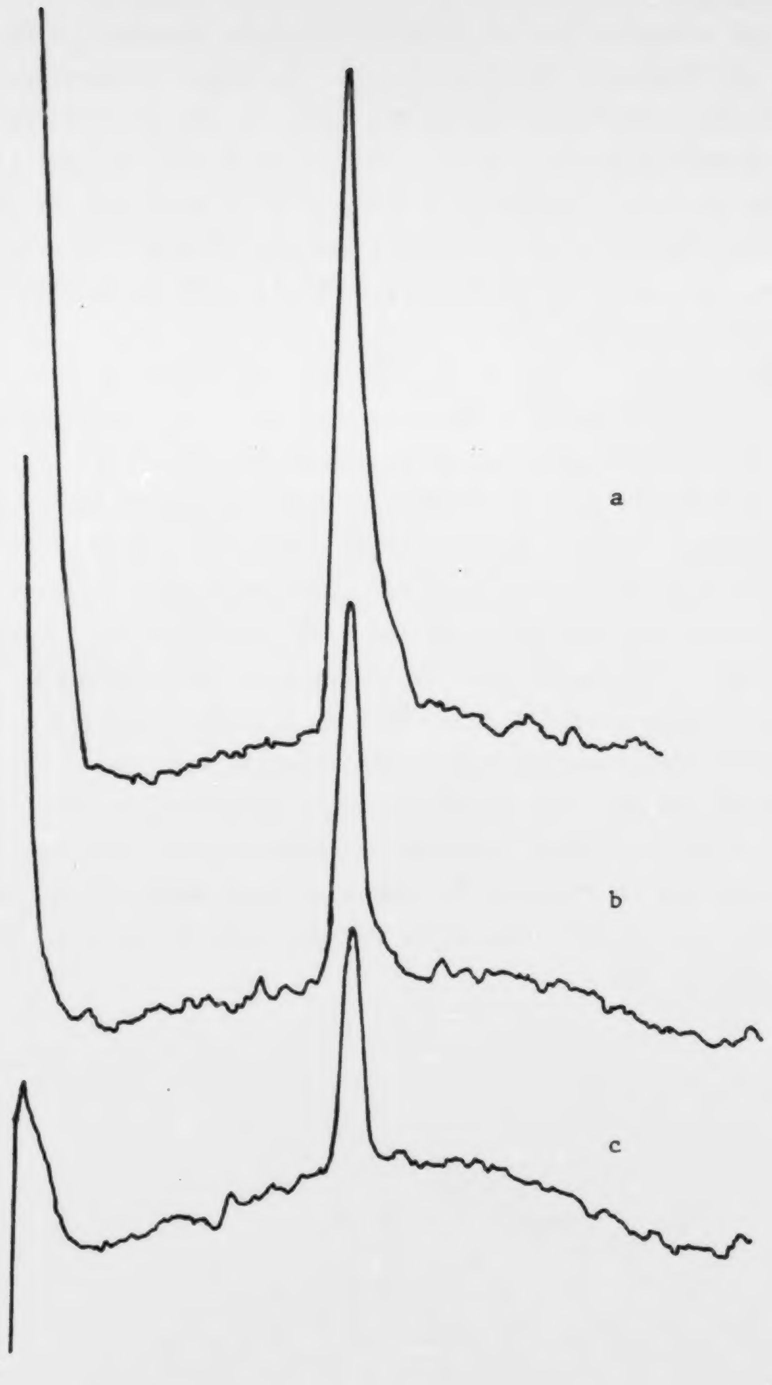


Figure L3. Thin layer chromatograms of Decabromobiphenyl ether on silica gel fluorescence quench mode: a. 500 ng Decabrom, b. 200 ng Decabrom, c. 100 ng Decabrom.

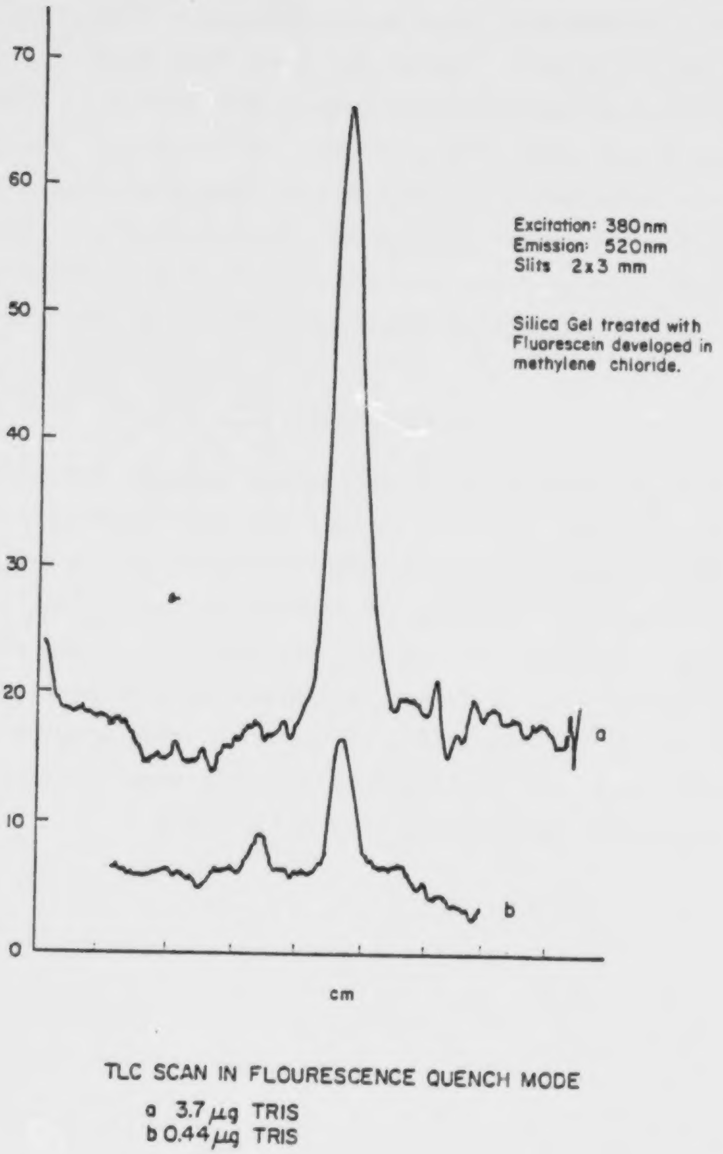


Figure L4. Thin layer chromatogram of tris(2,3-dibromopropyl)-phosphate on fluorescein impregnated silica gel, solvent: methylene chloride. Scan in fluorescence quench mode. a. 3.7 μg TRIS, b. 0.44 μg TRIS.

M. OZONE MEASUREMENTS

INSTRUMENTATION

Ambient ozone concentrations were measured using a Bendix Model 8002 chemiluminescent ozone analyzer. The Bendix Model 8002 ozone analyzer (S/N 301469-1) is an EPA Designated Reference Model (RFOA-0176-007) and was operated on the 0-0.5 ppm range with a 40-sec time constant. The principle of operation of this instrument is based on the flamess gas-phase chemiluminescent reaction between ethylene and ozone. The reliability, stability, specificity, and precision of ozone measurements by this reference method have been adequately demonstrated in numerous studies and described in the literature.

CALIBRATION

Dynamic multipoint calibration of the Bendix analyzer was accomplished by use of an ultraviolet ozone generator that was referenced to a NBS-SRM (NO in nitrogen) by gas phase titration with excess ozone. Normal gas phase titration could not be used, due to failure of the NO_x analyzer that is required for this procedure. A complete description of this procedure is provided separately. Primary dynamic calibrations were performed on the analyzer prior to and at the conclusion of the monitoring program. Daily zero and span checks were also performed by the instrument operator to assure adequate instrument performance on a daily basis.

CALIBRATION PROCEDURE USING GAS PHASE TITRATION WITH EXCESS O_3

Major equipment required:	Stable ozone generator
	NO concentration standard
	Ozone Analyzer
	Strip chart recorder, and
	Bubble flowmeter or wet test meter

1. Principle

1.1 The calibration procedure is based upon the rapid gas phase reaction between ozone (O_3) and nitric oxide (NO) in accordance with the following equation: (1)

$$NO + O_3 \rightarrow NO_2 + O_2$$

The quantitative nature of this reaction is such that the amounts of NO and O_3 reacted are equivalent. Nitric oxide is added to O_3 in a dynamic system, and the chemiluminescent O_3 analyzer being audited is used as an indicator of changes in O_3 concentration. The decrease in O_3 response indicator of changes in O_3 concentration. The decrease in O_3 response observed on analyzer is equivalent to the concentration of NO added. By measuring this decrease in response and the initial response, the O_3 concentration can be determined. Additional O_3 concentrations are generated by a dilution technique. The dynamic system is designed to produce locally high concentrations of O_3 and NO in the reaction chamber, with subsequent dilution, to insure complete NO reaction with relatively small chamber volumes. Errors can result if flow conditions in the dynamic calibration system are not correct. Erroneous results can also occur if the analyzer response is non-linear.

2. Apparatus

Figure M1 a schematic of a typical GPT apparatus, shows the suggested configuration of the components listed below. All connections between components in the calibration system downstream from the O_3 generator should be glass or Teflon. Additional information regarding the assembly of a GPT calibration apparatus is given in Reference (2).

2.1 Air flow controllers. Devices capable of maintaining constant air flow within +2%.

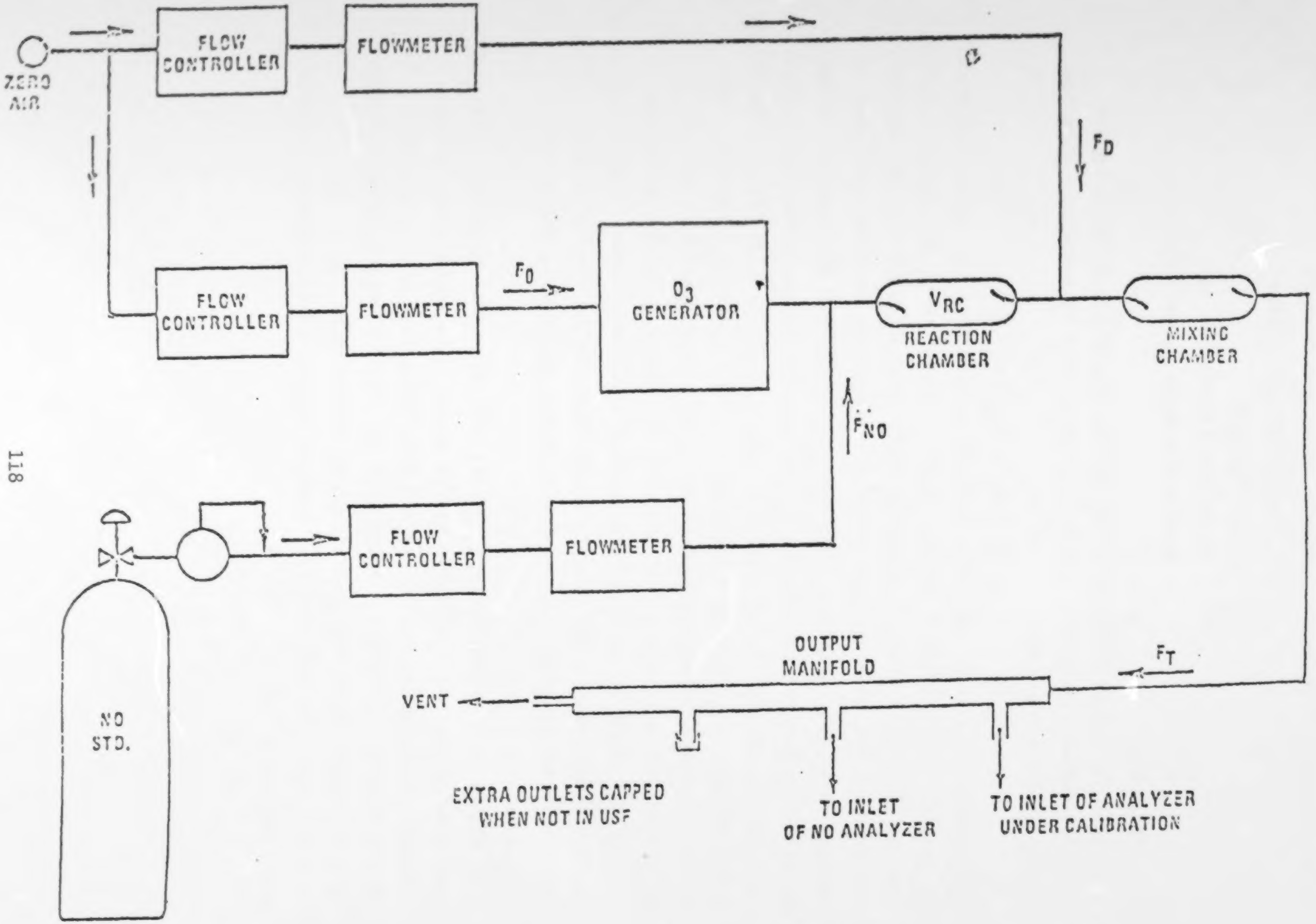

ZERO AIR
FLOW CONTROLLER
FLOWMETER
F_D
FLOW CONTROLLER
FLOWMETER
F_O
O_3 GENERATOR
V_{RC}
REACTION CHAMBER
MIXING CHAMBER
F_{NO}
NO STD.
FLOW CONTROLLER
FLOWMETER
OUTPUT MANIFOLD
F_T
VENT
EXTRA OUTLETS CAPPED WHEN NOT IN USE
TO INLET OF NO ANALYZER
TO INLET OF ANALYZER UNDER CALIBRATION

Figure M1. Schematic diagram of a typical GPT calibration system.

2.2 NO flow controller. A device capable of maintaining constant NO flow within ±2%. Component parts in contact with the NO must be of a non-reactive material.

2.3 Air flowmeters. Properly calibrated flowmeters capable of measuring and monitoring air flows within ±2%.

2.4 NO flowmeter. A properly calibrated flowmeter capable of measuring and monitoring NO flows within ±2%. (Rotameters have been reported to operate unreliably when measuring low NO flows and are not recommended.)

2.5 Pressure regulator for standard NO cylinder. This regulator must be non-reactive internal parts and a suitable delivery pressure.

2.6 Ozone generator. Capable of generating a stable level of O_3 at the flow rates required (see 4).

2.7 Reaction chamber. A glass chamber for the quantitative reaction of NO with excess O_3. The chamber should be of sufficient volume (V_{RC}) such that the residence time (t_R) is as specified in 4.

2.8 Mixing chamber. A glass chamber of proper design to provide thorough mixing of reaction products and diluent air. The residence time is not critical when the dynamic parameter specifications given in 4 are met.

2.9 Output manifold. The output manifold should be constructed of glass or Teflon of sufficient diameter to insure a minimum pressure drop at the analyzer connection. The system must have a vent designed to insure atmospheric pressure at the manifold and to prevent ambient air from entering the manifold.

3. Reagents

3.1 NO concentration standard. Cylinder containing 50 to 100 ppm NO in N_2. The cylinder must be traceable to a National Bureau of Standards NO in N_2 Standard Reference Material (SRM 1629). The cylinder (working standard) should be recertified on a regular basis as determined by the local quality control program. (See Reference (2).

3.2 Zero Air. Air, free of contaminants which will cause a detectable response on the O_3 analyzer or which might react with either NO or O_3 in the gas phase titration. A procedure for generating zero air is given in Reference (2).

4. Dynamic Parameter Specifications

4.1 The residence time (tR) in the reaction chamber and the gas flows (F_O and F_{NO}) (see Figure 1) must be adjusted according to the following relationships:

$$P_R = [O_3]_{RC} \times t_R = 1.5 \text{ ppm-minutes}$$

$$[O_3]_{RC} = [O_3]_{OUT} \left(\frac{F_T}{F_O + F_{NO}} \right)$$

$$t_R = \frac{V_{RC}}{F_O + F_{NO}}$$

where

P_R = Dynamic specifications, determined empirically, to insure complete reaction of NO, ppm-minutes

$[O_3]_{RC}$ = O_3 concentration in the reaction chamber, ppm

t_R = Residence time in the reaction chamber, minutes

$[O_3]_{OUT}$ = 80% URL concentration of O_3 at the output manifold, ppm

F_T = Total flow at the output manifold, scm^3/min

F_O = Ozone generator air flow, scm^3/min

F_{NO} = NO flow, scm^3/min

V_{RC} = Volume of the reaction chamber, scm^3.

4.2 These parameters may be selected according to the following sequences:

(a) Determine F_T, the total flow required at the output manifold (F_T = analyzer(s) demand plus 10% to 50% excess).

(b) Determine $[O_3]_{OUT}$ as the 80% URL (upper range limit) concentration required at the output manifold.

(c) Determine F_{NO} as

$$F_{NO} = \frac{0.8 \times [O_3]_{OUT} \times F_T}{[NO]_{STD}}$$

where:

$[NO]_{STD}$ = Concentration of the undiluted NO standard, ppm.

(d) Select a convenient or available reaction chamber volume. Initially, a trial V_{RU} may be selected to be in the range of approximately 300 to 1500 scm^3.

(e) Computer F_O as

$$F_O = \sqrt{\frac{[O_3]_{OUT} \times F_T \times V_{RC}}{1.5}} - F_{NO}$$

(f) Compute t_R as

$$t_R = \frac{V_{RC}}{F_O + F_{NO}}$$

(g) Compute F_D as

$$F_D = F_T - F_O - F_{NO}$$

where:

FD = Diluent air flow, scm^3/min.

(h) If F_O turns out to be impractical for the desired system, select a reaction chamber having a different V_{RC} and recompuete F_O and F_D. For a more detailed discussion of these requirements and other related considerations as well as example calculations, reference to Reference (2). A procedure for the initial checkout of the GPT system and the dynamic parameter specifications given above is also included in Reference (2).

5. Procedure

5.1 Assemble a dynamic calibration system such as shown in Figure 1.

5.2 Establish the dynamic parameters as indicated in 4. Use a bubble flowmeter or wet test meter to measure flow through the generator (F_O) and total flow out (F_T). Record F_0 and F_T on the data sheet. Record generator flow controller setting on the data sheet.

5.3 Insure that all flowmeters are properly calibrated under the conditions of use against a reliable standard such as a soap-bubble meter or wet-test meter traceable to NBS. All volumetric flow rates should be corrected to 25°C and 760 torr. Flow rates measured with a wet test meter or bubble flowmeter should be corrected for water vapor pressure. The corrected flow rate can be determined as shown below.

$$F_m \left[\left(\frac{P_A - P_W}{P_{STD}}\right) \left(\frac{T_{STD}}{T_A}\right)\right] = F_C$$

where:

F_m = flow rate as measured with a bubble flowmeter or wet test meter
P_A = ambient air pressure
P_M = water vapor pressure
P_{STD} = standard pressure 760.0 torr at 29.92" Hg
T_A = ambient temperature °K
T_{STD} = standard temperature °K = 298
F_C = corrected flow rate.

A detailed discussion on proper calibration of flowmeters is given in Reference (2).

5.4 Precautions must be taken to remove O_2 and other contaminants from the NO pressure regulator and delivery system prior to the start of calibration to avoid any conversion of the standard NO to NO_2. Failure to do so can cause significant errors in calibration. This problem may be minimized by (1) carefully evacuating the regulator, when possible, after the regulator has been connected to the cylinder and before opening the cylinder valve; (2) thoroughly flushing the regulator and delivery system with NO after opening the cylinder valve; (3) not removing the regulator from the cylinder between calibrations unless absolutely necessary. Further discussion of these procedures is given in Reference (2).

5.5 Allow sufficient time for the O_3 analyzer to warmup and stabilize. Adjust the diluent air and O_3 generator air flows to obtain the flows determined in step 4.2. Record the O_3 generator air flow (F_0), O_3 generator flow control setting and total flow out (F_T). The total air flow ($F_0 + F_{NO} + F_D = F_T$) must exceed the demand of the analyzer under calibration to insure that no ambient air is pulled into the manifold vent. Advance the recorder chart a couple of inches from the last ambient air trace and allow the O_3 analyzer to sample zero air until a stable response is obtained. Record the unadjusted recorder response (Z_u) for calibration zero air and for interval zero. Record analyzer response to internal span.

5.6 Adjust the O_3 generator to generate an O_3 concentration of approximately 80% of the URL as measured on the O_3 analyzer. When the response has stabilized, record as I_{80}.

5.7 Turn the NO flow on and ajust until the O_3 analyzer response has been decreased by 75-80 percent of its original value. For example, if I_{80} = 80% of URL, the NO flow should be adjusted to give a resultant analyzer response of 16-20% of the URL. When the resultant response has stabilized, record as I.

5.8 Measure the NO flow and record as F_{NO}. Record the cylinder NO concentration and flow control setting on the data sheet.

5.9 Calculate the exact NO concentration from:

$$[NO] = \frac{F_{NO} \times [NO]_{STD}}{R_{NO} + F_0 + F_D}$$

where:

[NO] = Diluted NO concentration, ppm

5.10 Calculate the O_3 concentration from:

$$[O_3]_{OUT} = \frac{I_{80}}{\left(I_{80} \times \frac{F_C + F_D}{F_{NO} + F_0 + F_D}\right) - I} \times [NO]$$

where:

$[O_3]_{OUT}$ = O_3 concentration, ppm

I_{80} = Original O_3 analyzer response, % chart

I = Resultant O_3 analyzer response after addition of NO, % chart (10) is usually small and may be ignored by using equation (11).

5.11 Record calculations on the data sheet.

Remove the NO flow. The O_3 analyzer response should return to its original value. Record the unadjusted response I_{80}. Calculate the percent audit error and record the PAE.

$$(PAE)_{80} = \frac{R(\%\text{ chart} - Z_U)}{[O_3]_{80}} - 100$$

where:

PAE = Percent Audit Error

R = Full Scale Range

% chart = Percent chart recorder response to O_3

$[O_3]_{80}$ = O_3 concentration, ppm, generated at 80% URL

Z_U = % recorder response for zero offset.

5.12 Adjust the dilution blow control to give an O_3 concentration of 60% URL. Using a soap-bubble meter or wet-test meter, measure the new total air flow at the outlet of the calibrator. Record the total air flow (F_1), NO flow control setting and dilution flow control setting.

$$[O_3]_{Gen} = [O_3]_{80} \times \frac{F_O + F_D}{F_O}$$

where:

$[O_3]_{60}$ = 60% URL O_3 concentration, ppm

$[O_3]_{80}$ = 80% URL O_3 concentration, ppm

F_0 = original total air flow, cm^3/minute

F_1 = total air flow upon dilution, cm^3/minute

Record calculations and the recorder response (I_{60}) on the data sheet.

5.13 Calculate the percent audit error and record the PAE.

$$(PAE)_{60} = \frac{R(\%\ \text{chart} - Z_U)}{[O_3]_{60}} - 100$$

5.14 Readjust dilution flow to give the original total air flow (F_0).

5.15 Adjust the UV lamp setting on the O_3 generator to give an O_3 concentration of approximately 40% of the URL and repeat the RGPT procedures (steps 5.6 through 5.13) substituting I_{40} for I_{80}.

5.16 Adjust the dilution flow to give a total on O_3 concentration of 20% URL. Using a soap bubble meter or wet-test meter, measure the total air flow at the outlet of the calibrator. Record the total air flow (F_2) on the data sheet. Calculate the diluted O_3 concentration ($[O_3]_{20}$] from:

$$F_{ND} = \frac{0.8 \times [O_3]_{OUT} \times F_T}{[NO]_{STD}}$$

$$F_0 = \sqrt{\frac{[O_3]_{OUT} \times F_T \times V_{RC}}{1.5}} - F_{NO}$$

$$t_R = \frac{V_{RC}}{F_0 + F_{NO}}$$

$$[O_3]_{RC} = [O_3]_{OUT} \left(\frac{F_T}{F_0 + F_{NO}} \right)$$

$$P_R = [O_3]_{RC} \times T_R = 1.5 \text{ ppm min}$$

$$F_D = F_t - F_0 - F_{NO}$$

$$[NO] = \frac{F_{NO} \times [NO]_{STD}}{F_{NO} + F_O + F_D}$$

$$[O_3]_{OUT} = \frac{I_0}{I_0 \times \left(\frac{F_O + F_D}{F_{NO} + F_O + F_D}\right) - 1} \times [NO]$$

$$[O_3]_{GEN} = [O_3]_{OUT} \left(\frac{F_O + F_D}{F_O}\right)$$

$$[O_3]_{OUT} = [O_3]_{GEN} \left(\frac{F_O}{F_O + F_D}\right)$$

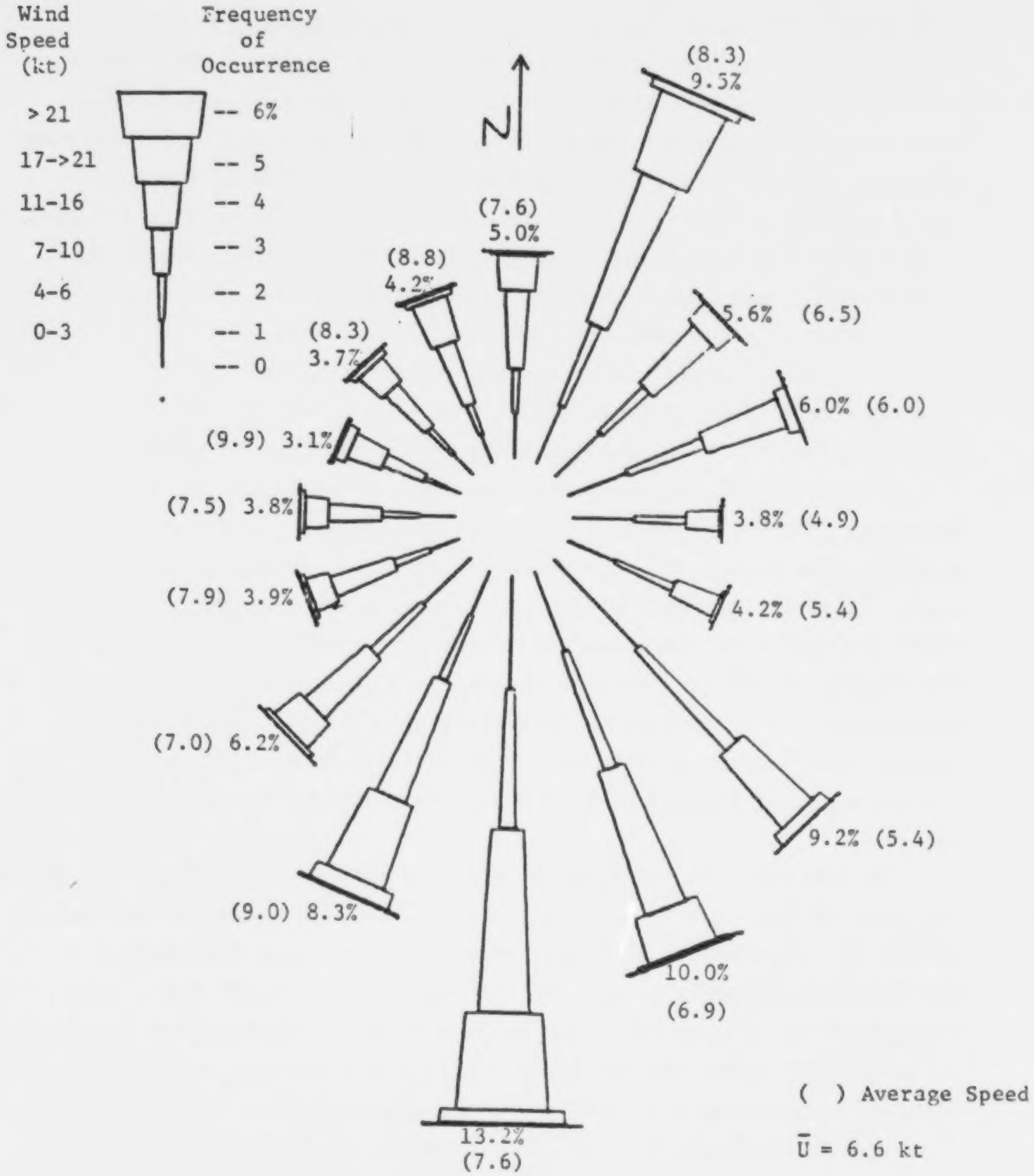
SECTION B: ATMOSPHERIC DISPERSION MODELING

ATMOSPHERIC DISPERSION MODELING

An assessment of both long and short-term dispersion patterns was made to assist in developing sampling strategies and in understanding the vegetation damage indicated by the analyses of infrared photographs of the study area. The long-term assessment used the Climatological Dispersion Model (CDM) and the short-term assessment used the Point-Multiple Model (PTMPT) of EPA's UNAMAP Library. These models use known area and point emissions and observed meteorological conditions (of wind speed, wind direction, and stability category) to estimate the concentration which would occur at selected sampling locations. The CDM considers area and point emissions (annual average) of one or two pollutants. The computations are made independently of one another. In this application, emission rates for various materials at each of the three bromine extraction plants in the vicinity of El Dorado, Arkansas were obtained through the Project Officer. The hydrogen sulfide emissions inventory was thought to be the most realible, so H_2S was chosen as one pollutant for modeling. An ideal, non-reactive gas which, hypothetically, was emitted in equal amounts from each of the three plants, was also selected for modeling. While none of the inventoried emissions were uniform from plant to plant, the latter choice gives some insight into the meteorological impacts and the source distribution impacts on estimated concentrations.

Meteorological data for El Dorado were obtained through the National Climatic Center, Asheville, N. C. Those data classify the frequency of occurrence of six wind speed categories, sixteen wind direction categories and five atmospheric stability categories on the basis of hourly weather observations made between January 1950 and December 1954. The frequency of occurrence of wind direction and speed (for all categories of atmospheric stability) was developed and is shown in Figure B1. North-northeasterly winds and southerly winds are the most predominant. Northwesterly winds are infrequency but strong; southeasterly winds are generally light.

The CDM requires six stability categories--four of which are characteristic of daytime conditions, and two which characterize nighttime



ANNUAL WIND ROSE

El Dorado, Arkansas

1950 - 1954

Figure B1

conditions. The fourth category of the data available from NCC is characteristic of stable conditions during night and day. This fourth category was subdivided into a stable-day and a stable-night category. Since winds are generally higher in daytime than at night, the stable-day category included 40 percent of the occurrence of winds of the lower wind speed categories ($\leq$ 7 kt) and 60 percent of the occurrence of winds in the remaining wind speed categories regardless of their direction. In this way, a new fourth category (stable-day), a new fifth category (stable-night), and a new sixth (the available fifth, very stable-night) category were developed. Source characteristics assumed for the pollutants are given in Table B1. An average air temperature of 15°C and mixing depths of 450 m (night) and 1491 m (day) were assumed.

Average annual concentrations and average concentrations for September to November were estimated by the model at 2 km intervals on a square grid encompassing the three plant sites and the surrounding area. Isopleths of equal concentration were drawn from those estimates. These analyses were then drawn as overlays of the USGS maps portraying the vegetation damage. Visual inspections showed no discernable relationship of the concentration distribution to the vegetation damage. Indeed, that damage occurred most frequently along power line rights of way and railroad tracks, both of which are periodically cleared of vegetation.

The CDM was also run to model a single point source of unit emissions for both the Fall and Annual stability-wind relationships. Those results showed the preparedness of higher concentrations along the north-south axis and displaced slightly to the west of the source. In the Fall season, the concentrations tend to be larger because of slower wind speeds. (Figures B1,B2).

The PTMPT model was run for a single source of unit emission and the observed meteorology for May 10, 1976 as a sample date. This day picked from readily available data as characteristic of conditions which could occur during the early fall. Stability was estimated using Turner's method. Calm winds were assigned a random direction and an 0.5 m/s speed to overcome the model's inability to treat calm conditions.

Table B1. Source Characteristics

Source	Emission Rates tons/year P1	P2	Source Height (m)	Height Diameter (m)	Exit Velocity (m/s)	Exit Temperature (C)
1	10.23	1.0	10	2	5	50
2	0.404	1.0	10	2	5	50
3	13.43	1.0	10	2	5	50

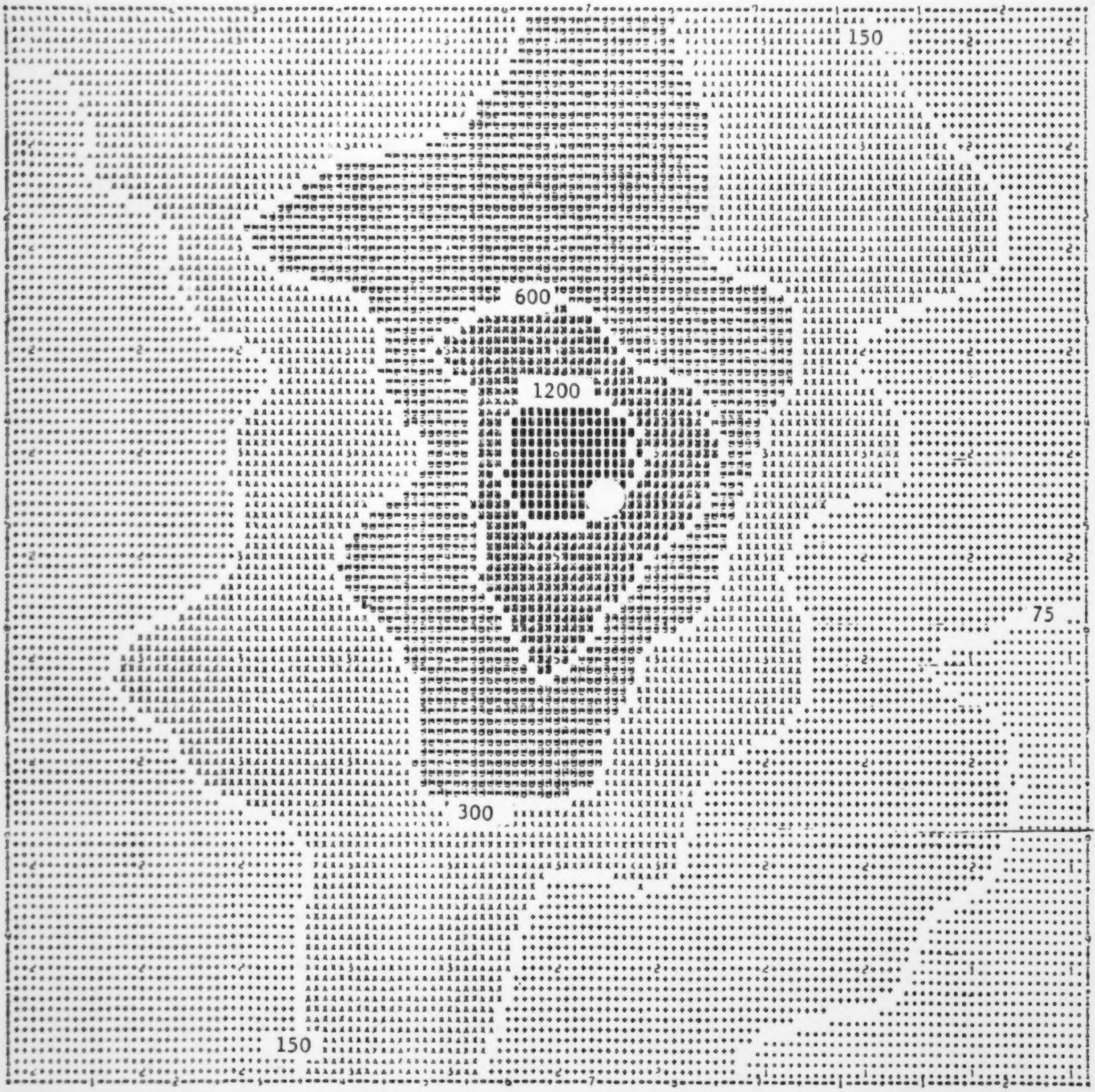


Figure B2. Annual Average concentration ($\mu g/m^3$) of an inert pollutant emitted at a rate of 1 gm/sec in the El Dorado, Arkansas vicinity. Open circle indicates source. Overall scale dimensions are 25 km x 25 km.

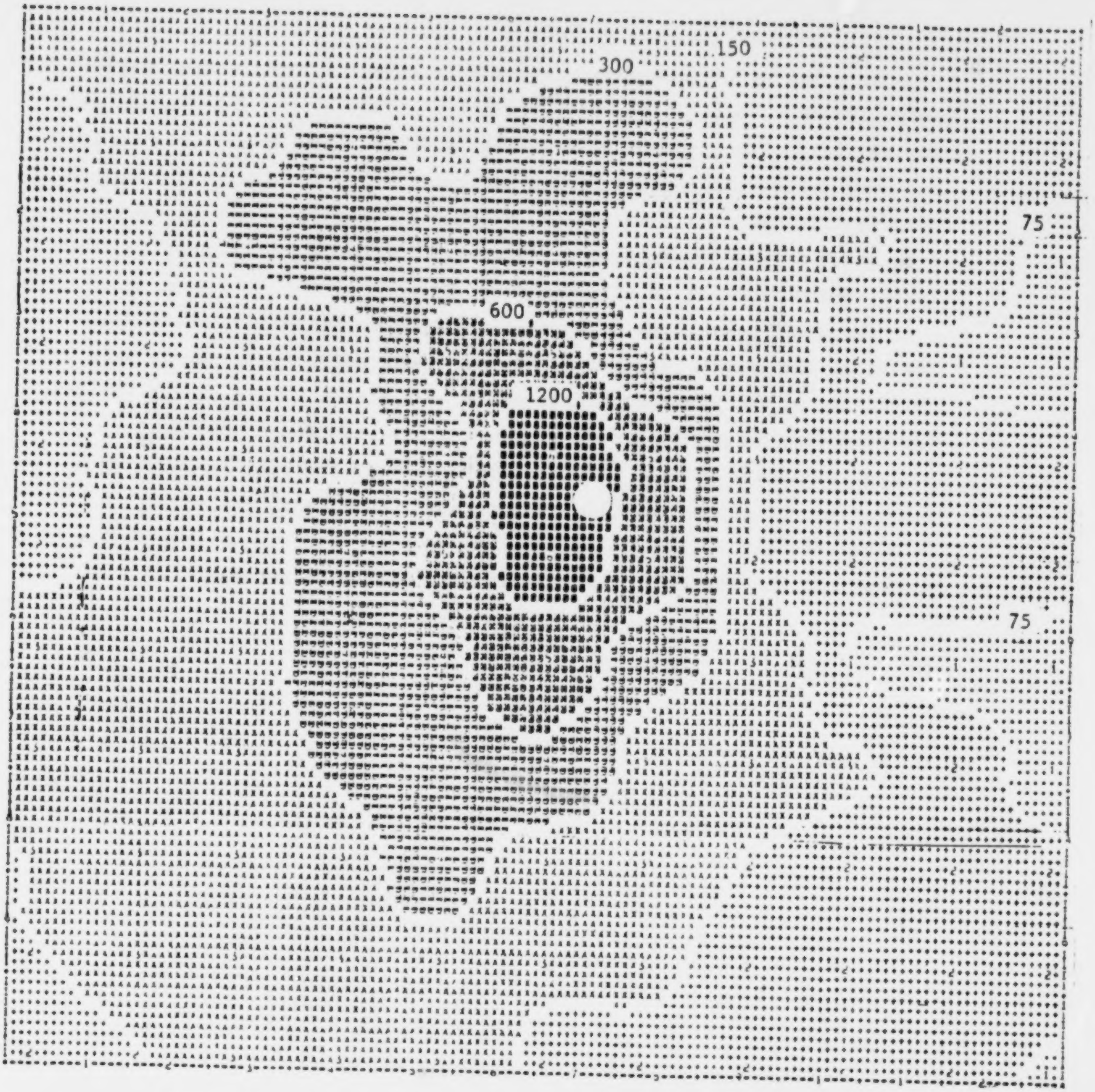


Figure B3. Average concentration for autumn ($\mu g/m^3$), of an inert pollutant emitted at a rate of 1 gm/sec in the El Dorado, Arkansas vicinity. Open circle indicates the source. Overall scale dimensions are 25 km by 25 km.

An array of 24 receptor points was developed. Eight points were established at 45-deg intervals, beginning at North at a 1 km radius from the emitter. Eight points were similarly established as the 2 km radius but were rotated 15 degrees clockwise from North. The last eight points were established at a 4 km radius, rotated 15 degrees counterclockwise from North. This arrangement of receptors was designed to intercept at least some portion of an effluent plume.

The PTMPT model runs were unsatisfactory at estimating the source impact at the chosen receptor locations. Generally, the plume is barely detectable at two receptor points and make a strong impact at one receptor The summation of hourly impacts to give a distribution of the daily average pollutant gives a very distorted view of the real impact. This fault lies a) in the sampling network used, and b) in the model. It does strongly indicate that sampling in the immediate vicinity of an emitter can be extremely sensitive to wind direction changes.

SECTION C: METEOROLOGICAL DATA

METEOROLOGICAL DATA (JULY 18-AUGUST 12, 1977)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed	
7/18/77	0100	75	72	1017.9	--	--	
	0200	76	72	1017.1	--	--	
	0300	76	72	1017.9	--	--	
	0400	74	72	1017.9	--	--	
	0500	74	72	1018.3	--	--	
	0600	74	71	1018.6	--	--	
	0700	78	74	1019.3	--	--	
	0800	84	73	1019.6	--	--	
	0900	88	72	1019.6	--	--	
	1000	92	71	1019.3	--	--	
	1100	94	71	1018.9	090	05	
	1200	95	72	1018.6	040	05	
	1300	98	70	1017.7	090	10	
	1400	98	67	1017.1	080	10	915
	1500	99	68	1016.0	090	10	
	1600	98	68	1016.1	120	07	
	1700	97	67	1015.8	100	10	
	1800	94	69	1016.1	130	09	
	1900	91	71	1015.8	150	05	
	2000	87	71	1016.1	180	04	
	2100	85	71	1016.8	--	--	
	2200	82	71	1016.8	--	--	
	2300	80	71	1017.1	--	--	
	2400	78	71	1017.1	--	--	

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/20/77	0100	76	72	1016.0	--	--
	0200	76	73	1016.0	--	--
	0300	76	73	1016.0	170	04
	0400	77	73	1016.0	180	04
	0500	77	73	1016.6	150	04
	0600	77	73	1016.8	--	--
	0700	77	73	1017.6	190	05
	0800	80	75	1017.9	230	04
	0900	83	75	1017.9	260	05
	1000	85	75	1018.2	290	06
	1100	85	75	1017.9	--	--
	1200	87	75	1017.9	100	07
	1300	76	71	1017.9	100	06
	1400	80	74	1017.2	190	05
	1500	82	75	1017.2	120	05
	1600	85	76	1016.4	130	07
	1700	84	74	1016.4	200	05
	1800	83	74	1016.8	190	04
	1900	82	75	1016.4	130	04
	2000	80	75	1016.4	--	--
	2100	79	74	1017.2	--	--
	2200	78	74	1017.2	--	--
	2300	77	72	1017.9	--	--
	2400	75	72	1017.9	--	--

24 hr precipitation - 0.18 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/21/77	0100	75	72	1018.3	130	03
	0200	76	74	1018.3	130	03
	0300	76	74	1017.9	160	08
	0400	76	73	1018.3	170	04
	0500	76	73	1019.0	170	04
	0600	76	73	1019.6	200	04
	0700	76	73	1020.0	190	03
	0800	78	75	1019.9	200	05
	0900	80	76	1020.0	220	05
	1000	85	76	1020.4	260	07
	1100	89	76	1020.3	210	08
	1200	91	77	1019.6	210	06
	1300	84	75	1018.6	010	08
	1400	82	76	1018.9	350	10
	1500	88	76	1017.7	350	05
	1600	90	74	1017.4	100	05
	1700	89	76	1017.0	120	04
	1800	88	77	1016.7	120	04
	1900	86	77	1016.7	120	05
	2000	84	76	1017.4	130	04
	2100	81	76	1017.7	--	--
	2200	79	75	1017.7	--	--
	2300	79	75	1018.2	--	--
	2400	78	75	1017.9	--	--

24 hr rainfall - 0.67 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/22/77	0100	78	75	1017.9	--	--
	0200	78	75	1017.5	--	--
	0300	77	74	1017.5	--	--
	0400	77	74	1017.9	--	--
	0500	76	73	1018.2	--	--
	0600	76	73	1019.0	--	--
	0700	79	75	1019.0	--	--
	0800	83	76	1019.4	300	04
	0900	88	76	1019.0	010	04
	1000	91	75	1019.0	020	04
	1100	94	74	1018.6	310	06
	1200	96	73	1018.2	300	06
	1300	92	73	1017.4	230	10
	1400	97	72	1016.4	--	--
	1500	97	76	1016.1	300	08
	1600	96	74	1015.4	--	--
	1700	95	74	1015.1	320	06
	1800	89	73	1015.5	030	04
	1900	91	78	1015.8	170	09
	2000	86	75	1016.1	--	--
	2100	82	75	1016.9	--	--
	2200	81	76	1016.8	--	--
	2300	80	75	1016.8	210	04
	2400	79	74	1016.8	--	--

24 hr rainfall - 0

(continued)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/23/77	0100	78	74	1016.9	--	--
	0200	78	74	1016.5	--	--
	0300	77	74	1016.5	--	--
	0400	76	73	1016.5	--	--
	0500	76	74	1016.9	--	--
	0600	77	73	1017.7	--	--
	0700	80	75	1018.0	--	--
	0800	85	76	1018.0	--	--
	0900	88	76	1018.3	--	--
	1000	91	76	1018.3	130	03
	1100	94	76	1017.4	200	07
	1200	96	76	1017.1	040	04
	1300	96	77	1016.4	030	05
	1400	98	74	1015.4	320	05
	1500	98	74	1015.4	--	--
	1600	99	72	1015.1	240	04
	1700	95	77	1015.4	070	10
	1800	89	76	1014.9	--	--
	1900	85	79	1015.8	--	--
	2000	84	77	1015.9	--	--
	2100	84	76	1015.9	--	--
	2200	82	77	1015.5	--	--
	2300	81	77	1015.8	--	--
	2400	80	76	1016.1	--	--

24 hr rainfall - trace

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/24/77	0100	80	77	1015.8	--	--
	0200	80	76	1015.8	--	--
	0300	80	76	1015.4	--	--
	0400	79	76	1015.0	--	--
	0500	79	76	1015.4	--	--
	0600	78	76	1016.5	--	--
	0700	81	77	1016.1	180	04
	0800	84	79	1016.5	210	05
	0900	85	79	1016.5	220	05
	1000	91	79	1016.0	180	04
	1100	94	79	1016.0	110	05
	1200	96	79	1015.4	180	07
	1300	99	79	1014.7	220	06
	1400	98	74	1013.7	310	08
	1500	92	77	1013.7	200	07
	1600	88	76	1013.3	200	10
	1700	86	75	1014.3	180	05
	1800	83	76	1014.7	120	10
	1900	82	77	1015.1	130	04
	2000	81	77	1015.1	100	05
	2100	80	76	1015.1	120	05
	2200	80	76	1015.4	120	04
	2300	79	75	1015.1	160	04
	2400	78	75	1014.7	--	--

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/25/77	0100	78	74	1014.4	190	05
	0200	78	74	1014.4	200	04
	0300	77	74	1014.4	--	--
	0400	77	74	1014.5	--	--
	0500	78	74	1014.9	--	--
	0600	78	75	1015.2	170	05
	0700	81	76	1015.9	200	06
	0800	84	78	1016.2	230	08
	0900	90	78	1016.6	250	08
	1000	93	77	1016.2	270	10
	1100	95	76	1015.8	240	06
	1200	99	75	1015.4	190	08
	1300	101	75	1014.8	190	07
	1400	100	77	1014.0	180	07
	1500	86	79	1014.8	100	15 (G22)
	1600	83	76	1014.0	170	07
	1700	85	80	1014.1	170	05
	1800	85	79	1014.1	170	06
	1900	84	78	1013.8	170	07
	2000	83	78	1014.8	140	03
	2100	81	77	1015.2	130	04
	2200	80	76	1015.8	220	03
	2300	80	76	1014.2	--	--
	2400	79	75	1015.4	--	--

24 hr precipitation - 0.17 inch

(continued

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/26/77	0100	78	75	1016.4	050	10
	0200	79	76	1017.4	060	13
	0300	77	72	1017.8	050	15
	0400	75	72	1016.5	--	--
	0500	75	72	1016.]	260	09
	0600	75	72	1016.5	100	05
	0700	75	73	1017.9	050	04
	0800	78	74	1019.0	360	05
	0900	79	74	1019.4	320	04
	1000	84	75	1019.4	060	07
	1100	87	75	1019.0	070	06
	1200	91	79	1018.5	040	08
	1300	91	75	1018.5	050	05
	1400	92	75	1017.8	030	08
	1500	92	75	1017.4	010	09
	1600	92	76	1016.9	030	07
	1700	90	78	1016.9	010	11
	1800	86	76	1016.9	050	12
	1900	85	76	1016.9	070	06
	2000	82	77	1016.1	120	05
	2100	80	77	1016.9	--	--
	2200	79	77	1017.7	010	06
	2300	79	77	1018.1	020	04
	2400	79	77	1017.8	040	04

24 hr precipitation - 0.29 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/27/77	0100	78	76	1017.8	030	04
	0200	78	76	1017.2	030	05
	0300	77	76	1017.2	030	04
	0400	77	75	1016.8	030	06
	0500	75	73	1017.2	050	05
	0600	75	73	1017.6	--	--
	0700	75	73	1018.3	--	--
	0800	75	73	1018.3	010	04
	0900	76	73	1018.6	00	00
	1000	80	74	1018.3	--	--
	1100	83	75	1017.9	--	--
	1200	87	75	1017.2	--	--
	1300	90	75	1015.6	210	05
	1400	78	74	1017.3	030	12
	1500	76	71	1016.9	250	03
	1600	75	-	1015.8	250	04
	1700	76	-	1015.0	--	--
	1800	76	-	1015.0	--	--
	1900	77	77	1015.4	--	--
	2000	77	77	1015.4	--	--
	2100	76	76	1015.8	--	--
	2200	76	76	1016.2	--	--
	2300	76	76	1016.2	350	05
	2400	77	77	1016.2	360	04

24 hr precipitation - 1.15 inches

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/28/77	0100	77	77	1016.2	--	--
	0200	77	77	1015.8	--	--
	0300	77	77	1015.8	350	04
	0400	76	76	1016.2	310	04
	0500	76	76	1016.8	310	04
	0600	76	76	1016.8	320	04
	0700	77	77	1017.4	--	--
	0800	78	78	1017.6	230	05
	0900	81	81	1017.9	--	--
	1000	83	80	1017.9	260	04
	1100	81	80	1018.3	270	04
	1200	81	80	1018.3	220	05
	1300	80	80	1017.5	180	05
	1400	85	80	1017.1	210	06
	1500	85	80	1016.5	240	05
	1600	86	-	1016.2	180	04
	1700	85	-	1015.5	230	05
	1800	85	-	1015.5	180	05
	1900	84	-	1015.8	140	03
	2000	81	-	1015.8	--	--
	2100	80	-	1016.7	170	03
	2200	79	-	1017.2	--	--
	2300	79	-	1016.5	170	03
	2400	78	1017.2		--	--

24 hr precipitation - 0.11 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/29/77	0100	79	-	1016.8	--	--
	0200	79	-	1016.5	--	--
	0300	78	-	1016.5	--	--
	0400	-	-	1016.5	--	--
	0500	78	-	1016.8	--	--
	0600	78	-	1016.8	--	--
	0700	79	-	1017.3	190	04
	0800	81	-	1017.5	190	05
	0900	83	-	1017.5	210	05
	1000	84	-	1017.9	210	07
	1100	-	-	1017.5	240	07
	1200	-	-	1017.3	230	09
	1300	-	-	1016.9	230	07
	1400	88	75	1016.1	250	06
	1500	89	74	1015.5	190	05
	1600	89	72	1015.5	270	05
	1700	87	75	1015.5	200	06
	1800	86	76	1015.8	010	04
	1900	83	76	1015.8	--	--
	2000	82	76	1015.8	--	--
	2100	80	74	1016.4	--	--
	2200	79	73	1016.9	--	--
	2300	78	72	1016.5	210	05
	2400	76	71	-	210	05

(continued)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/30/77	0100	75	71	1015.8	--	--
	0200	75	71	1015.8	--	--
	0300	75	71	1015.4	--	--
	0400	74	70	1015.8	--	--
	0500	74	71	1016.2	--	--
	0600	74	70	1016.5	--	--
	0700	76	71	1016.9	180	05
	0800	81	73	1016.9	230	07
	0900	80	72	1017.3	240	07
	1000	76	72	1017.9	230	08
	1100	75	71	1017.9	210	04
	1200	75	71	1017.6	200	04
	1300	77	73	1016.9	190	05
	1400	80	74	1015.5	160	06
	1500	80	73	1015.2	180	05
	1600	80	74	1014.9	200	05
	1700	81	74	1014.9	--	--
	1800	81	75	1014.5	--	--
	1900	80	75	1014.1	--	--
	2000	79	75	1013.5	--	--
	2100	77	74	1014.1	--	--
	2200	77	74	1014.5	--	--
	2300	77	74	1014.5	--	--
	2400	77	74	1014.5	--	--

24 hr precipitation - 0.10 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/31/77	0100	76	74	1014.1	--	--
	0200	76	74	1013.3	--	--
	0300	76	74	1013.3	200	04
	0400	76	74	1013.7	230	06
	0500	76	73	1014.5	230	04
	0600	76	72	1016.0	250	03
	0700	77	73	1016.0	270	04
	0800	82	75	1015.7	220	07
	0900	83	72	1015.7	--	--
	1000	85	72	1016.0	220	07
	1100	84	70	-	260	05
	1200	82	69	1016.2	260	06
	1300	77	69	1016.5	290	08
	1400	80	73	1015.1	230	07
	1500	86	70	1014.1	250	06
	1600	90	69	1013.8	250	06
	1700	90	71	1013.8	230	05
	1800	89	71	1013.4	210	04
	1900	82	75	1014.5	--	--
	2000	80	75	1014.5	--	--
	2100	78	74	1015.1	--	--
	2200	77	73	1015.5	--	--
	2300	77	73	1015.9	--	--
	2400	76	72	1015.5	--	--

24 hr precipitation - 0.09 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
8/1/77	0100	75	72	1015.1	--	--
	0200	75	72	1015.5	340	04
	0300	75	72	1015.9	340	05
	0400	74	69	1016.2	340	13
	0500	72	68	1019.0	270	15
	0600	71	66	1020.0	260	09
	0700	71	66	1017.9	230	11
	0800	74	67	1015.9	--	--
	0900	74	67	1017.2	030	12
	1000	75	67	1018.3	010	05
	1100	78	67	1018.3	020	06
	1200	82	74	1017.9	020	07
	1300	84	67	1017.5	350	09
	1400	84	67	1017.3	030	07
	1500	82	69	1016.5	030	04
	1600	81	70	1016.2	--	--
	1700	82	70	1016.2	100	05
	1800	82	70	1016.2	--	--
	1900	79	71	1016.2	--	--
	2000	75	71	1016.5	--	--
	2100	72	69	1016.8	--	--
	2200	71	68	1017.1	--	--
	2300	71	68	1017.1	--	--
	2400	70	67	1017.2	--	--

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
8/2/77	0100	69	67	1016.9	--	--
	0200	68	66	1016.5	--	--
	0300	69	66	1016.2	340	04
	0400	68	65	1016.2	350	05
	0500	68	66	1016.9	--	--
	0600	68	66	1016.9	350	04
	0700	70	67	1017.2	010	05
	0800	73	69	1017.6	340	03
	0900	79	69	1017.2	120	04
	1000	82	70	1016.9	030	05
	1100	86	70	1017.2	040	04
	1200	85	69	1017.2	050	05
	1300	88	69	1016.6	030	07
	1400	90	65	1015.8	040	07
	1500	90	64	1015.2	040	05
	1600	90	64	1014.9	080	07
	1700	90	61	1014.9	040	06
	1800	88	62	1014.9	040	05
	1900	79	66	1014.9	--	--
	2000	74	66	1015.0	--	--
	2100	72	65	1015.5	--	--
	2200	69	64	1015.9	--	--
	2300	68	63	1015.9	--	--
	2400	66	62	1016.2	--	--

(continued)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
8/3/77	0100	65	61	1016.2	--	--
	0200	63	60	1016.2	--	--
	0300	63	60	1016.2	--	--
	0400	62	60	1016.2	--	--
	0500	63	60	1016.2	--	--
	0600	63	60	1016.5	--	--
	0700	67	63	1016.9	--	--
	0800	74	65	1016.8	--	--
	0900	81	63	1017.2	--	--
	1000	84	61	1017.5	070	05
	1100	86	63	1017.5	040	05
	1200	89	64	1017.2	060	08
	1300	90	64	1016.1	050	06
	1400	91	64	1016.1	090	07
	1500	92	61	1015.5	040	05
	1600	92	62	1015.1	070	07
	1700	92	62	1014.8	100	07
	1800	91	64	1014.8	130	04
	1900	82	68	1015.6	--	--
	2000	74	68	1016.0	--	--
	2100	72	66	1016.6	--	--
	2200	70	65	1017.0	--	--
	2300	69	64	1016.6	--	
	2400	68	64	1016.1	--	--

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
8/4/77	0100	67	63	1015.9	--	--
	0200	67	63	1015.5	--	--
	0300	66	63	1015.1	--	--
	0400	66	62	1014.8	--	--
	0500	66	62	1015.5	--	--
	0600	65	52	1017.2	--	--
	0700	70	66	1017.9	--	--
	0800	75	69	1018.2	080	04
	0900	81	71	1017.9	180	04
	1000	86	71	1017.5	150	04
	1100	88	70	1017.5	140	05
	1200	90	69	1017.2	090	06
	1300	90	68	1016.5	040	08
	1400	90	69	1015.9	070	05
	1500	92	67	1015.9	090	08
	1600	92	66	1015.1	150	09
	1700	90	67	1015.1	150	08
	1800	90	68	1015.1	130	06
	1900	86	68	1015.5	140	06
	2000	83	70	1015.9	130	07
	2100	80	72	1016.7	160	04
	2200	78	71	1017.5	130	05
	2300	77	71	1017.9	130	05
	2400	77	71	1017.8	140	06

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
8/5/77	0100	76	71	1017.2	140	06
	0200	75	71	1017.5	140	05
	0300	76	72	1017.5	140	05
	0400	76	72	1017.5	140	06
	0500	77	72	1018.2	160	05
	0600	77	72	1019.3	160	05
	0700	78	73	1020.0	160	07
	0800	79	73	1020.3	170	07
	0900	82	74	1020.3	160	09
	1000	82	73	1020.3	150	08
	1100	85	73	1019.9	150	09
	1200	86	71	1019.1	160	06
	1300	88	72	1018.8	140	06
	1400	87	71	1018.0	090	06
	1500	88	71	1017.2	130	08
	1600	75	71	1019.3	200	10
	1700	76	72	1018.6	170	05
	1800	76	72	1018.6	160	07
	1900	75	72	1019.0	190	04
	2000	74	72	1019.6	--	--
	2100	74	71	1020.0	090	04
	2200	73	71	1019.6	--	--
	2300	73	71	1019.6	120	04
	2400	73	71	1019.6	120	04

24 hr precipitation - 0.25 inch

(continued)

SECTION C (cont'd)

Date	Time	Temperature (°F)	Dew Point	Pressure	Wind Direction (°)	Speed
7/19/77	0100	77	71	1016.8	--	--
	0200	76	71	1016.5	--	--
	0300	76	71	1016.5	--	--
	0400	75	70	1016.8	--	--
	0500	74	70	1016.8	--	--
	0600	74	70	1017.2	--	--
	0700	75	70	1017.8	--	--
	0800	75	72	1018.2	100	04
	0900	76	73	1018.2	--	--
	1000	79	74	1018.2	--	--
	1100	80	75	1017.8	--	--
	1200	84	76	1017.5	350	05
	1300	88	75	1017.1	070	04
	1400	89	74	1015.8	060	03
	1500	90	74	1015.4	150	04
	1600	91	73	1014.8	--	--
	1700	85	71	1015.1	320	06
	1800	80	72	1015.1	060	08
	1900	79	73	1015.1	100	06
	2000	77	73	1015.5	080	05
	2100	77	73	1015.5	--	--
	2200	77	73	1015.9	--	--
	2300	76	72	1016.3	--	--
	2400	76	72	1016.3	--	--

24 hr precipitation - 0.19 inches

(continued)

SECTION D: HOURLY OZONE CONCENTRATIONS IN EL DORADO, ARKANSAS

HOURLY OZONE CONCENTRATIONS IN EL DORADO, ARKANSAS

Site Location: Arkansas Chemical - El Dorado, Arkansas

Charts Read by: Mark Saeger

Time: Central Standard Time

Date Hour	7/22/77	7/23/77	7/24/77	7/25/77	7/26/77	7/27/77
01	-	0.010	0.003	0.012	0.010	0.010
02	-	0.008	0.008	0.017	0.005	0.012
03	-	0.005	0.005	0.015	0.017	0.005
04	-	0.003	0.000	0.012	0.052	0.005
05	-	0.003	0.000	0.010	0.042	0.005
06	-	0.003	0.003	0.008	0.032	0.000
07	-	0.003	0.003	0.008	0.040	0.005
08	-	0.008	0.005	0.012	0.035	0.005
09	-	*	0.015	0.025	0.030	0.008
10	-	0.030	*	*	*	*
11	-	0.040	0.040	0.050	0.027	*
12	-	0.035	0.047	0.057	0.032	0.020
13	-	0.042	0.060	0.060	0.035	0.022
14	-	0.045	0.065	0.062	0.042	0.032
15	-	0.047	0.060	0.062	0.040	0.035
16	C	0.047	0.057	0.052	0.047	0.037
17	C	0.042	0.052	0.042	0.037	0.032
18	C	0.045	0.047	0.037	0.020	0.030
19	0.032	0.035	0.042	0.037	0.015	0.027
20	0.027	0.012	0.037	0.035	0.025	0.015
21	0.040	0.010	0.020	0.027	0.030	0.010
22	0.027	0.017	0.022	0.010	0.022	0.012
23	0.012	0.008	0.027	0.012	0.012	0.010
24	0.008	0.003	0.020	0.012	0.010	0.005

- Instrument not on-line.

C - Initial calibration.

* - Zero/span.

Date	7/28/77	7/29/77	7/30/77	7/31/77	8/01/77	7/02/77
Hour						
01	0.003	0.005	0.022	0.005	0.000	0.000
02	0.000	0.003	0.012	0.003	0.000	0.000
03	0.000	0.005	0.008	0.003	0.000	0.000
04	0.003	0.000	0.008	0.005	0.000	0.000
05	0.003	0.000	0.010	0.008	0.010	0.000
06	0.008	0.003	0.008	0.008	0.037	0.003
07	0.008	0.003	0.005	0.008	0.040	0.000
08	0.010	0.010	0.010	0.005	0.037	0.003
09	0.012	0.015	0.017	0.012	0.035	0.008
10	0.022	*	*	0.022	0.017	0.028
11	**	0.022	0.027	0.030	0.020	0.038
12	**	0.030	0.027	0.030	0.015	0.043
13	**	0.040	0.030	0.025	0.018	0.035
14	**	0.050	0.030	0.027	0.028	0.030
15	**	0.050	0.030	0.035	0.028	0.038
16	0.037	0.050	0.032	0.035	0.025	0.033
17	0.040	0.050	0.027	0.040	*	0.033
18	0.042	0.050	0.025	0.040	0.023	0.025
19	0.042	0.027	0.020	*	0.018	*
20	0.035	0.017	0.017	0.010	0.018	0.023
21	0.015	0.015	0.012	0.005	0.005	0.015
22	0.008	0.022	0.003	0.000	0.003	0.005
23	0.000	0.020	0.003	0.000	0.000	0.000
24	0.000	0.022	0.005	0.000	0.000	0.003

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* - Zero/span.

** - EPA audit.

Date	8/03/77	8/04/77	8/05/77	8/06/77	8/07/77	8/08/77
Hour						
01	0.000	0.000	0.022	0.015	0.005	0.005
02	0.000	0.000	0.020	0.013	0.005	0.003
03	0.000	0.000	0.020	0.010	0.000	0.003
04	0.000	0.000	0.022	0.008	0.003	0.000
05	0.000	0.000	0.025	0.003	0.003	0.000
06	0.000	0.000	0.022	0.000	0.000	0.000
07	0.000	0.000	0.020	0.000	0.000	0.000
08	0.000	0.003	0.017	0.003	0.005	0.003
09	0.025	0.017	0.020	0.015	0.012	0.015
10	0.087	0.037	0.022	0.025	0.017	0.025
11	0.082	0.045	0.025	0.030	0.022	0.035
12	0.072	0.047	0.033	0.032	0.022	0.035
13	0.062	0.045	0.035	0.032	*	0.035
14	0.062	0.057	0.035	0.030	0.020	0.037
15	0.067	0.055	0.032	0.030	0.022	0.037
16	0.065	0.057	0.035	0.030	0.027	*
17	0.057	0.067	0.037	0.025	0.030	0.040
18	*	*	*	*	0.035	0.040
19	0.055	0.052	0.027	0.025	0.032	0.032
20	0.027	0.045	0.027	0.015	0.027	0.020
21	0.017	0.037	0.022	0.005	0.020	0.010
22	0.008	0.027	0.015	0.003	0.008	0.017
23	0.008	0.027	0.003	0.003	0.008	0.022
24	0.003	0.025	0.012	0.000	0.008	0.027

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* - Zero/span.

Date Hour	8/09/77	8/10/77	8/11/77	8/12/77
01	0.025	0.003	0.030	0.017
02	0.012	0.003	0.022	0.017
03	0.005	0.003	0.017	0.015
04	0.003	0.005	0.022	0.010
05	0.008	0.003	0.015	0.010
06	0.005	0.000	0.008	0.010
07	0.000	0.000	0.005	0.010
08	0.005	0.003	0.008	0.005
09	0.015	0.008	0.017	0.012
10	0.025	0.017	0.027	0.017
11	0.030	0.022	0.030	0.022
12	0.035	*	0.030	0.027
13	0.042	0.040	0.035	0.032
14	0.045	0.045	0.035	0.032
15	0.045	0.045	0.042	0.020
16	*	0.047	0.047	0.027
17	0.045	0.042	*	*
18	0.042	0.047	0.045	0.037
19	0.032	0.077	0.040	0.040
20	0.020	0.065	0.035	0.040
21	0.010	0.047	0.030	0.032
22	0.003	0.040	0.022	0.027
23	0.000	0.042	0.025	0.022
24	0.000	0.035	0.017	0.015

* - Zero/span.